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Review of Control Strategies for Ozone and Their Effects on Other Environmental Issues

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This review summarizes t[illegible]cal, experimental, field and modeling data related to effects of reducing volati[illegible]ic compounds (VOC), oxides of nitrogen (NO_x) or both for meeting the ambien[illegible]uality standard for ozone (O_3). Implications are reviewed for several environmental concerns. These include O_3 levels within and immediately downwind of major sources of precursors (i.e., cities), O_3 concentrations in rural/remote areas, ambient levels of nitrogen dioxide (NO_2), acidic species formation and visibility attenuation.

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Review Of Control Strategies For Ozone And Their Effects On Other Environmental Issues

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Air Management Technology Branch
Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards

November 1986

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EXECUTIVE SUMMARY

The purpose of this report is to review scientific information in order to identify implications of reducing emissions of Volatile Organic Compounds (VOC) and/or Oxides of Nitrogen (NO_x) to achieve National Ambient Air Quality Standards (NAAQS) for ozone (O_3). Such a review is intended to serve as background information which can be utilized by U.S. Environmental Protection Agency (EPA) policymakers. Therefore, the review is one source of information for those charged with formulating appropriate strategies to reduce O_3.

The primary strategy recommended by the U.S. EPA to attain the O_3 NAAQS is to reduce VOC emissions. A considerable amount of experimental/modeling/monitoring information has become available since the strategy was first formulated. This information sheds light not only on relationships between VOC and NO_x control and reductions in O_3, but relationships between VOC and NO_x control strategies and emerging environmental issues like acid deposition and visibility attenuation as well.

Consequences of reducing VOC versus NO_x are examined with regard to five environmental issues. These issues include:

(1) O_3 concentrations in an urban plume within one day's (i.e., 10 hours) travel time (at prevailing wind velocities) of a city;

(2) O_3 in rural/remote locations which may not be impacted by an urban plume emanating from a city within 10 hours of travel time;

(3) peak and mean concentrations of Nitrogen Dioxide (NO_2);

(4) formation of acid species [nitric acid (HNO_3) and sulfuric acid (H_2SO_4)] in the ambient air; and

(5) deterioration of regional visibility.

Each of these issues is first discussed at some length. The review concludes by (a) identifying potential implications regarding the effects of VOC and NO_x control on each of the five issues identified above, and (b) identifying information needs and appropriate studies for fulfilling them.

Issue (1): One Day Ozone Problem

Relative effectiveness of VOC versus NO_x controls in reducing peak O_3 concentrations in an urban plume depends on a number of factors. These include the prevailing NMOC*/NO_x ratio, severity of the existing O_3 concentrations, reactivity of the NMOC mix and, in some cases, atmospheric dilution. A VOC strategy is more efficient as the NMOC/NO_x ratio decreases, reactivity of the NMOC mix decreases, severity of an O_3 problem increases, and dilution increases. At ratios below about 10:1, for typical NMOC compositions and under a wide variety of conditions, modeling studies indicate that relatively greater reductions in NO_x than in VOC are needed to attain the NAAQS.

A VOC strategy has other potential advantages over an NO_x strategy as well. One possible consequence of an NO_x strategy is to cause peak O_3 concentrations to occur closer to the most heavily populated areas. This occurs primarily because nitric oxide (NO) emissions tend to occur in the most heavily populated areas. The most immediate effect of NO emissions is to quench O_3. Only after a period of several hours are conditions favorable for O_3 accumulation. Hence, until the NAAQS is actually attained, an NO_x strategy carries with it the potential for increasing population exposure to O_3 concentrations above the level of the NAAQS. In contrast, a VOC strategy should delay accumulation of O_3. This occurs because NMOC provides the principal means of oxidizing NO so as to promote buildup of O_3. Lower concentrations of NMOC delay this process. The result of this delay is a lowering of O_3 concentrations throughout the most heavily populated areas.

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*Non-methane organic compounds. Ambient concentrations of VOC are commonly referred to as "NMOC." This convention is followed in this review.

For cities with NMOC/NO_x ratios about 10-20:1, we enter a gray area in which sensitivity tests performed with the Empirical Kinetic Modeling Approach (EKMA) model suggest that in some cases strategies incorporating VOC and NO_x reductions could be more effective in reducing peak O_3 than a strategy emphasizing VOC reductions only. That is, under some conditions, such a strategy may result in earlier reductions in O_3 then would be true for a VOC only strategy, with only small differences in the ultimate VOC control target needed to meet the NAAQS. Which strategy is most effective depends on the specific situation.

In cases where the NMOC/NO_x ratio is typically greater than about 20:1, it is possible that a strategy emphasizing NO_x control would be more effective than a VOC strategy in attaining the NAAQS. One concern about such a NO_x control strategy however is that it may increase population exposure to high O_3 before the NAAQS is attained. This latter feature may impose practical limitations on the implementation of an NO_x strategy, so that it would be viable only for cities which already have low concentrations of NO_x.

In the absence of a city-specific demonstration that NO_x control is a more viable approach for attaining the O_3 NAAQS, a strategy emphasizing VOC control should remain the strategy of choice. Whether or not some supplementary control of NO_x would be beneficial is best determined on a case-by-case modeling investigation. This report does not adequately cover costs attendent with VOC versus NO_x control. However, it is generally believed that the cost associated with large NO_x reductions is greater than that for major VOC controls. Hence, the "equal control" NMOC/NO_x ratios discussed later in this report are likely to overestimate the attractiveness of NO_x control strategies. Further, a VOC strategy appears less risky, in view of modeling results which indicate the potential for strategies emphasizing NO_x control to increase temporarily the population exposure to O_3 levels above that specified in the NAAQS.

Issue (2): Rural Ozone

It is concluded that observed O_3 concentrations in rural/remote areas which are greater than 0.12 ppm are most often caused by urban plumes emanating from upwind urban areas less than 10 hours of travel time away. The most likely alternative explanations for high rural O_3 levels are: (1) generation from manmade precursors emitted in "rural" areas,* and (2) transport of urban O_3 aloft overnight and subsequent fumigation to the earth's surface on the second day. An urban NO_x strategy may be slightly more effective in reducing peak hourly O_3 concentrations in rural areas 10 or more hours travel time downwind from a city. This is likely because an NO_x strategy should reduce peak O_3 occurring closer to its city of origin. The resulting peak O_3 levels should, therefore, be subject to greater dilution before reaching rural/remote areas. However, transported NMOC has also been estimated to make the job of attaining the NAAQS in downwind cities more difficult under some circumstances. It is concluded that high O_3 in rural/remote areas resulting from urban plumes would be reduced regardless of whether an NO_x or VOC strategy is pursued in the urban area, so long as the strategy effectively reduces downwind peak O_3 concentrations. However, presently available information does not allow us to make an informed judgment as to whether a VOC strategy (with no NO_x reduction) could significantly exacerbate rural O_3 concentrations over longer averaging times or hourly O_3 concentrations which are presently well below the NAAQS.

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*According to the Agency's existing O_3 policy, a rural area can include small cities/towns with populations below 200,000.

The foregoing information indicates the Agency's current policy of giving higher priority to VOC controls in most urban areas is fundamentally sound. However, some flexibility could be maintained in deciding whether to pursue VOC or NO_x controls in each "rural" nonattainment area. It is generally believed that NMOC/NO_x ratios are higher in rural areas and in small cities than they are in urban areas. This should tend to make control of NO_x in such locations more attractive than it is for large urban areas. However, relative effectiveness of VOC versus NO_x strategies depends on reactivity of the NMOC mix, as well as the local NMOC/NO_x ratio. If the reactivity of a rural NMOC mix is much lower than that of a typical urban mix, this could favor a VOC strategy, all other factors being equal. Thus, the reactivity as well as the NMOC/NO_x ratio should be considered in assessing alternative strategies for reducing emissions in any "rural" area determined to be causing violations of the O_3 NAAQS.

Issue (3): Nitrogen Dioxide

Peak and mean concentrations of NO_2 can be diminished by reducing NO_x emissions. In contrast, reducing VOC appears to have only a small effect on peak NO_2 and little impact on mean concentrations. Thus, it appears that reducing NO_x is the only viable means for reducing NO_2 in areas which violate the Federal NAAQS for that pollutant. In some cases, locations pursuing a

VOC strategy for O_3 which are also in violation of both NAAQS for O_3 and NO_2, may need somewhat higher VOC controls than would otherwise be necessary to attain the O_3 NAAQS.

Issue (4): Acidic Species Formation

Acidic species formation and acid deposition have not been studied as long nor as extensively as the O_3 problem and major efforts to study the problem are currently underway. Consequently, judgments concerning the effect of VOC versus NO_x control on acid species must be more qualitative and tentative than those made in relation to the O_3 problem.

This study suggests that reducing NMOC has a small, ambiguous effect on the production of nitric acid (HNO_3) and sulfuric acid (H_2SO_4). However, reducing NO_x appears likely to lead to an approximately proportional reduction in the formation of HNO_3. The impact of NO_x strategies on H_2SO_4 formation is mixed, according to the best available estimates. NO_x reductions apparently lead to reductions in gas phase production of H_2SO_4 but to an increase in liquid phase H_2SO_4 formation. It is concluded that in the western U.S., where SO_2/H_2SO_4 is relatively small, NO_x reduction should most likely reduce formation of acidic species. In the eastern U.S., the impact of NO_x reduction on the concentrations of acidic species is less clear. Using the assumptions and models described in this paper, reducing NO_x will probably reduce acidic species formation in the East. The approximately proportional relationship with HNO_3 should outweigh any small increase in H_2SO_4 which might occur under some circumstances.

Issue (5): Visibility

Like the acid deposition problem, there remains considerable uncertainty regarding the impact of VOC and NO_x reductions on visibility. Conclusions are therefore not as strongly supported as those regarding ozone control. Regional visibility attenuation is primarily due to the formation of secondary particulates. In the eastern U.S., most of the reduction in regional visibility is thought to occur from the presence of sulfate ($SO_4^=$) aerosol. Sulfate aerosols occur primarily in two forms: as H_2SO_4 resulting from liquid phase formation, and as ammonium sulfate ($(NH_4)_2SO_4$) occurring primarily from the reaction of H_2SO_4 with naturally present ammonia (NH_3). In the presence of ample SO_2/ $SO_4^=$, reducing NO_x is likely to result in little improvement in visibility, and may even cause a slight deterioration (due to increased liquid phase formation of H_2SO_4). However, if vigorous programs are undertaken to reduce SO_2 (and $SO_4^=$), reduction in NO_x may lead to some further improvement in visibility. This latter improvement, if it occurs, would result from less HNO_3 being available to react with NH_3 to form nitrate (NO_3^-) aerosol. Using a similar argument, in the western U.S. (where there is little $SO_4^=$), reduction in NO_x may improve regional visibility. NO_x control would also improve visibility somewhat by reducing concentrations of NO_2. Control of certain species of NMOC should reduce the production of secondary organic aerosol. However, secondary organic aerosol is not believed to account for a major portion of regional visibility attenuation.

The review of acidic species formation and regional visibility attenuation suggests that control of NO_x may sometimes be beneficial. Hence, for some locations, the best strategies for dealing with these issues and for reducing O_3 may not always be compatible. In order to minimize any incompatibilities, selective control of NO_x to improve visibility or to reduce potential for acid deposition is suggested. This selection process entails: (a) control of elevated point sources of NO_x first in rural areas and then in other urban areas and (b) more general control of NO_x only in those urban areas using a strategy which features NO_x control to help reduce O_3 or NO_2.

Summary Of Strategy Implications

On the basis of the information reviewed in this report, the following strategy implications are derived.

1. A VOC control strategy is the most viable approach for attaining the O_3 NAAQS in cities having NMOC/NO_x ratios less than about 10:1.

2. For cities having typical mixes of NMOC and NMOC/NO_x ratios in the range of about 10-20:1, it is less certain that a VOC control strategy for reducing peak O_3 always will be superior to one which also includes some NO_x control. A strategy in which both VOC and NO_x are reduced may, in some cases, result in more rapid initial reductions in peak O_3 at the expense of slightly increasing the VOC reduction ultimately needed to attain the NAAQS. In other cases, VOC control needed to attain the NAAQS also may be reduced if there is some accompanying NO_x control. A case-by-case review is recommended to select the most appropriate strategy.

3. For cities with typical NMOC mixes and NMOC/NO_x ratios greater than about 20:1, it is possible that strategies emphasizing NO_x control may be most effective in attaining the O_3 NAAQS. However, the impact of such a strategy on population exposed to O_3, cost of controls and city-specific factors regarding reactivity of the NMOC mix, air quality and meteorology should be assessed prior to selecting a strategy in which NO_x control is emphasized (i.e., prior to relaxing any nationally applicable requirements for VOC regulation).

4. In the absence of a demonstration that an NO_x strategy is preferable, strategies emphasizing VOC control (with or without accompanying reductions in NO_x) should remain the ones of choice for reducing urban peak O_3 concentrations to the level of the NAAQS.

5. This review suggests that most rural hourly O_3 concentrations in excess of the NAAQS result from urban plumes. Therefore, strategies which reduce peak O_3 concentrations in urban plumes to the level of the NAAQS should also be effective in reducing the large majority of violations in rural areas.

6. Higher $NMOC/NO_x$ ratios in rural areas suggest that O_3 formation in such areas is limited by the availability of NO_x. Prior to considering an NO_x strategy for a rural area or small city believed to cause O_3 in excess of the NAAQS, however, attempts should be made to characterize the $NMOC/NO_x$ ratio and reactivity of the rural NMOC mix.

7. Control of NO_x emissions appears to be the only viable means for bringing areas violating the Federal NO_2 NAAQS into compliance. Thus, for cities violating the NAAQS or for cities subject to growth and having NO_2 concentrations near the NAAQS, some NO_x control may be necessary, even though in some cases it may increase VOC control requirements to meet the O_3 NAAQS.

8. The following conclusions with respect to acidic species and visibility are less certain and should be viewed more qualitatively.

a. Best available estimates suggest reducing NO_x will reduce HNO_3, but may, under some circumstances, increase H_2SO_4 somewhat. Thus, NO_x reduction appears likely to reduce acidic species levels in the western U.S. The picture is less clear in the East. For the given set of assumptions described in this review, it appears that reducing NO_x would lead to a reduction in acidic species formation in the eastern U.S. as well.

b. Although formation of acidic species is linked to the $NMOC/NO_x/O_3$ problem, current, but limited, studies available to us at this time suggest that VOC reduction may have little net effect on acidic species formation.

c. NO_x reduction appears likely to improve regional visibility in the West. In the East, however, little improvement in visibility is likely from NO_x control, unless and until substantial reductions in $SO_2/SO_4^=$ occur.

d. Optimum control strategies for O_3 may not be consistent with the most effective strategies for NO_2, acid deposition and visibility attenuation.

Informational Needs

Many of the strategy implications identified in this review are based on less than complete information. Therefore, a number of additional efforts have been identified which, if implemented, would improve the basis on which strategy/policy decisions concerning NO_x and VOC controls are made. These efforts include:

(a) a more complete and continuous characterization of $NMOC/NO_x$ ratios prevailing in urban and rural areas;

(b) incorporation and testing of rural chemistry in chemical kinetics mechanisms and in available models;

(c) more extensive simulations of VOC and NO_x control strategies with sophisticated photochemical models;

(d) more extensive evaluation and application of acidic species models, and

(e) a systematic assessment of available technology and costs associated with VOC and NO_x control so that economics can be more readily factored into decisions to choose a mix of VOC and NO_x controls for reducing O_3.

1.0 Introduction

Control of Volatile Organic Compounds (VOC) has been the U.S. Environmental Protection Agency's (EPA's) primary approach for reducing high ambient concentrations of ozone (O_3) to comply with National Ambient Air Quality Standards (NAAQS) for a number of years. Although Nitrogen Oxides (NO_x) are also widely recognized as precursors for O_3, control of NO_x has been undertaken principally to reduce ambient levels of Nitrogen Dioxide (NO_2) which exceed or approach NAAQS for NO_2. The purpose of this report is to review monitoring/modeling/experimental studies to identify implications of VOC versus NO_x controls to reduce ambient O_3. The report is intended to serve as a source of information to help decision makers weigh certain (but not all) environmental benefits/consequences of strategies which emphasize reducing VOC versus those which emphasize reducing NO_x. In addition, the report is intended to identify certain information gaps which, if filled, could provide a more informed basis for choosing the most desirable means to reduce O_3.

Implications of reducing VOC or NO_x emissions extend to other environmental concerns besides O_3 and NO_2. Acid deposition and visibility attenuation can be potentially affected by choice of strategies to reduce O_3 as well. This review, therefore, addresses the implications of VOC versus NO_x controls on the following five environmental issues:

1. Impact on O_3 concentrations occurring in urban plumes within one day's travel time (i.e., about 10 hours) downwind from cities;

2. Impact on O_3 concentrations greater than the NAAQS occurring in rural areas sometimes greater than 1 day's travel time downwind from major cities;

3. Impact on peak and mean concentrations of NO_2;

4. Effect on the formation of acidic species in the atmosphere; and

5. Effect on regional visibility attenuation.

There are several reasons why the review described in this report is timely. First, trends for O_3 reported in the National Air Quality and Emission Trends Report, 1984 (U.S. EPA, 1986) are not as pronounced as they are for several other pollutants which have been regulated over comparable time frames. It is appropriate to seek explanations for this finding. This review is one attempt to do so.

Second, information obtained from networks of Nonmethane Organic Compound (NMOC)* monitors deployed during the summers of 1984 and 1985 suggests higher typical NMOC/NO_x ratios than had previously been measured (Baugues (1986)). The new measurements were obtained using a method believed to be considerably more reliable than continuous techniques used in previous years. For example, Richter et al. (1985) report highly reproducible results which are also highly correlated with Gas Chromatographic (GC) sum-of-species results and exhibit only a small (8%) positive bias with respect to the latter. The median of median ratios measured in 23 cities was about 12:1. In 19 of the cities, median NMOC/NO_x ratios ranged from about 9-14:1. Thus, this range of ratios may be thought of as "typical" of median ratios obtained in the 1984-85 studies.† Thus, potential presence of higher than expected NMOC/NO_x ratios in several cities could make a review of the Agency's O_3 reduction strategy prudent.

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*In this report, NMOC and VOC are sometimes used interchangeably. Usually, however, NMOC is used to denote ambient concentrations, while VOC is used to denote emissions of organic compounds.

†Several small Gulf Coast cities were excluded in compiling these data. Data from these cities may be dominated by petrochemical facilities, report very low concentrations of NO_x and, therefore, higher NMOC/NO_x ratios.

Third, since the original VOC strategy was conceived, additional information in the form of modeling results, field and experimental data has become available. It is prudent to review this information in the context of current O_3 control strategies and other environmental concerns.

Decisions regarding appropriate strategies for reducing O_3, like many other environmental decisions, must be made in the presence of uncertainties. In order for the strategy implications identified in this review to be weighed properly by decision makers, it is appropriate to identify limitations in the underlying data base used to draw conclusions. One such limitation is that many of the cited references are not from the peer-reviewed open literature. It was necessary to cite several draft or internal reports, because only these have sufficient detail to allow one to draw conclusions regarding the efficacy of VOC and NO_x controls. Some of these papers describe work which is too recent to have appeared in peer-reviewed journals. Others were intended to serve as working level papers to define objectives for subsequent work, rather than as end products prepared specifically for publication.

A second limitation of the review is that it relies on modeling results which simulate relatively few days in relatively few cities. Particularly heavy reliance is placed on modeling results obtained for the Los Angeles area. Given the difficulty and expense of performing detailed modeling simulations, it makes sense that the most detailed information is available for the location where the O_3 problem is most severe. Although several other modeling studies appear to be in qualitative agreement with the Los Angeles results, the general applicability of the Los Angeles findings can be and has been questioned.

A third source of uncertainty results from the observation that predicted sensitivity of O_3 to changes in NMOC and/or NO_x depends on the chemistry assumed in the models. In this review, heavy reliance is placed on predictions made using carbon bond mechanisms (CB-2 and CB-3). While qualitative agreement exists between the carbon bond mechanisms and other chemical mechanisms used in the review (i.e., LIRAQ2 and Dodge), quantitative estimates are subject to some uncertainty.

Uncertainties about relationships between VOC and NO_x control strategies and changes in urban O_3 levels are smaller than those which relate to acid deposition and visibility attenuation. These latter two problems are more complex and have not been studied as extensively. As a result, conclusions related to acid deposition and visibility attenuation must be viewed more qualitatively and as preliminary. In reviewing potential consequences of VOC and NO_x control on acidic species formation and visibility, heavy reliance is placed on results of models which have undergone limited validation. Further, for acid deposition, model applications which are reviewed are limited in one case to clear sky and non-precipitating stratus cloud environments, and in a second case to one episode. Model inputs/assumptions appear reasonable in light of present knowledge, and the models appear to perform adequately in the limited tests to which they have been applied. Nevertheless, it is necessary to make a number of assumptions concerning appropriate model inputs. Further, it is not yet clear how important the situations simulated are relative to other environments in acidic species formation, nor is the relative importance of liquid vs. gas phase reactions in leading to acid deposition entirely understood.

Finally, it is well known that many species of VOC are toxic and certain compounds derived from NO_x may be potentially toxic as well. The desirability of controlling VOC or NO_x in order to reduce toxic species has not been addressed in this review.

This review is organized as follows.

Relationships between changes in NMOC and NO_x concentrations and high O_3 concentrations in an urban plume are discussed in Chapter 2.

Potential effects of control strategies on O_3 concentrations in excess of the NAAQS observed in rural areas are discussed in Chapter 3.

Chapter 4 addresses additional concerns, including the effect of VOC and NO_x controls on NO_2 and the role of NO_x and VOC emissions in contributing to acid deposition and visibility impairment. The review concludes by identifying a series of implications attendant with strategies to reduce O_3, as well as informational needs.

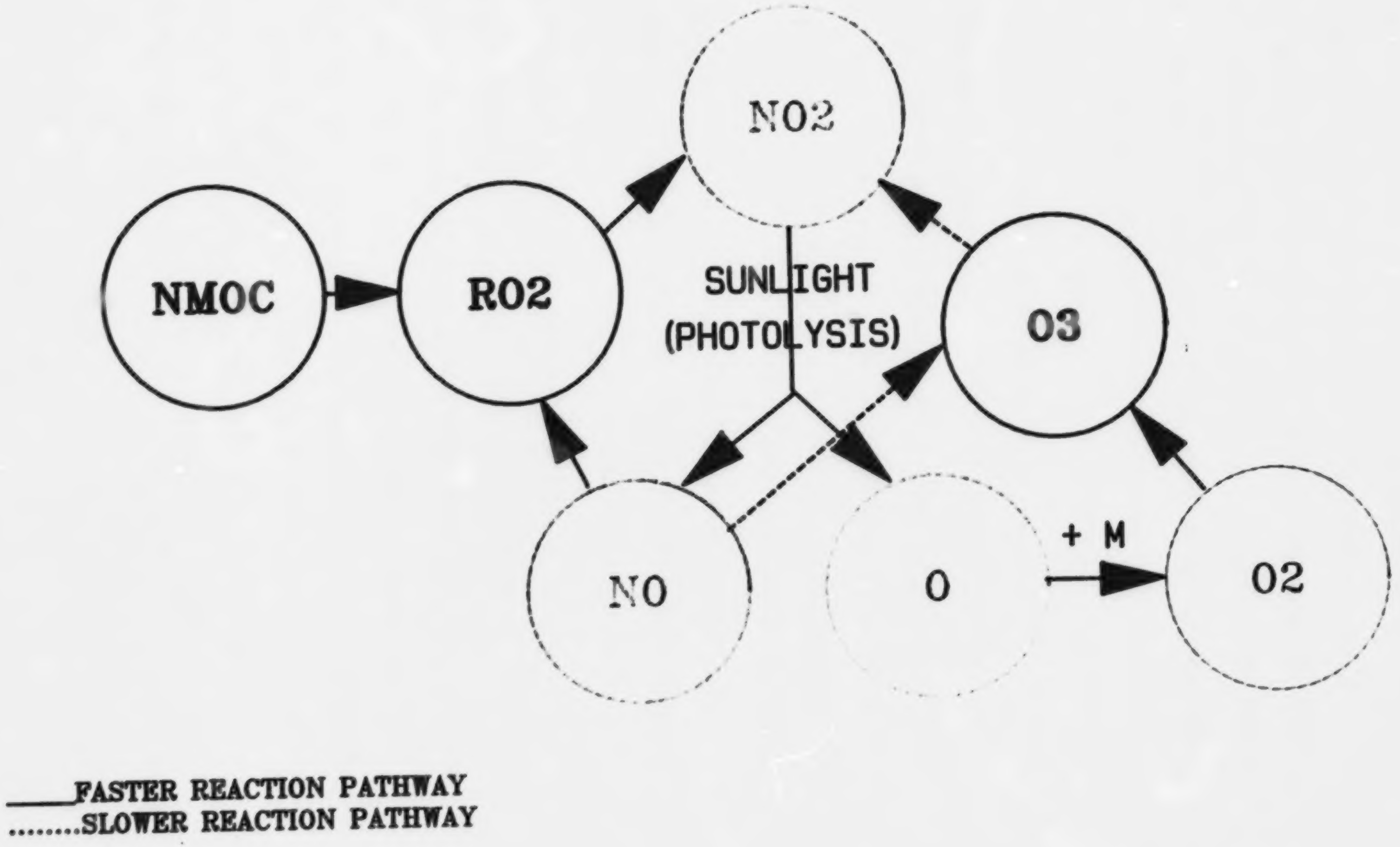
2.0 Maximum Ozone Concentrations: One Day Travel Time

High concentrations of O_3 observed in the vicinity of urban areas are a function of ambient concentrations of NMOC and NO_x (resulting from emissions occurring in the urban area and from transport of precursors from upwind sources), transport of O_3 from upwind areas, local meteorological conditions and location of the ambient O_3 monitors with respect to the city. NO_x provides the most important means by which O_3 forms. This occurs when NO_2 is photolyzed to form nitric oxide (NO) and an oxygen atom (O). The resulting oxygen atom combines rapidly with molecular oxygen (O_2) to form O_3. However, in the absence of other factors, the resulting O_3 disappears when it oxidizes the newly formed or fresh NO (the most abundant species of NO_x emitted by manmade sources) to reform NO_2. Hence, an equilibrium is established among NO, NO_2 and O_3 which prevents large buildup of O_3. The role of NMOC is to provide an alternate means (rather than O_3) of oxidizing NO to NO_2. Organics in the atmosphere undergo oxidation to form alkyperoxy free radicals (RO_2) which then oxidize NO to NO_2. Some of the resulting reaction products are themselves capable of oxidizing NO. The rate of oxidation of NO by some free radicals is thought to occur over 1000 times faster than the rate of oxidation by O_3. The result of these interactions between NMOC and NOx is that the presence of NMOC allows O_3 to accumulate to higher concentrations, and one molecule of NO_x can lead to several molecules of O_3 being formed as the result of repeated occurrences of the photolysis/oxidation cycle. Figure 1 illustrates the conceptual role of NMOC and NO_x in the formation and accumulation of O_3.

Meteorology affects the process described in the preceding paragraph in several ways. First, the rates of photolysis for NO_2 and certain other species are affected by sunlight intensity (e.g., latitude, time of year, cloud cover). Second, the rates for several key chemical reactions are also affected by temperature. Third, since O_3 levels depend on concentrations of its precursors, dilution resulting from prevailing meteorology can affect O_3 levels. Fourth, wind speed and direction determine whether a polluted air mass affects a monitoring site as well as the amount of reaction time available before the most heavily polluted air impacts a monitor.

Location of the ambient O_3 monitors determines the levels of O_3 which are observed in or near a city. Because of the usual diurnal patterns in temperature, sunlight intensity and emissions, peak O_3 concentrations are most likely to occur in the afternoon. Therefore, ambient monitoring sites

FIGURE 1
CONCEPTUAL DIAGRAM DEPICTING ROLES OF NOX AND ORGANICS IN FORMATION AND ACCUMULATION OF OZONE

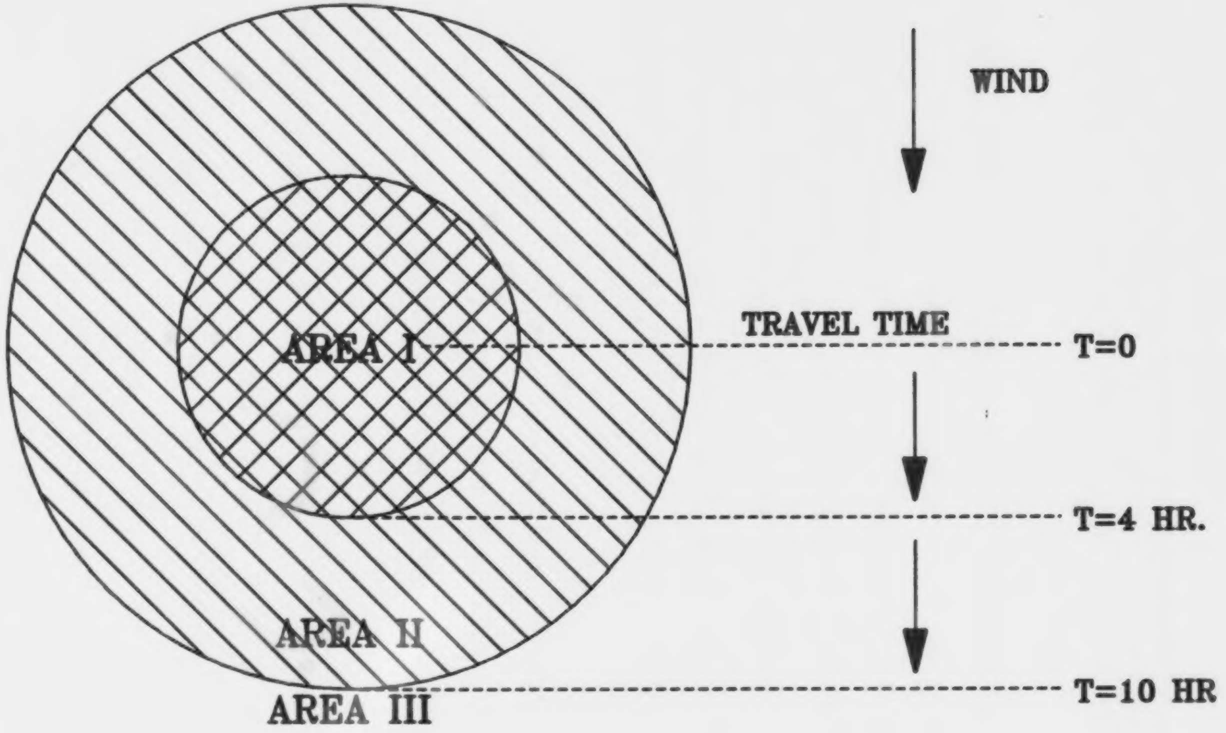

NMOC
R02
N02
SUNLIGHT
(PHOTOLYSIS)
03
N0
0
+ M
02
FASTER REACTION PATHWAY
SLOWER REACTION PATHWAY

observing highest levels of O_3 are typically those which the prevailing winds cause to be impacted by peak morning emissions during the afternoon.

Since the O_3 NAAQS is concerned with daily maximum concentrations, we often focus on sites which currently measure the daily maxima. However, in order to assess the implications of NO_x vs. VOC control strategies, it is important to review potential consequences at a variety of sites. Figure 2 is a conceptual representation of geographic zones within and downwind of a city. Area I is characterized by high VOC and NO_x emission densities typified by large central urban commercial/industrial districts. Area I is also often characterized by high population. Area II represents suburban or surrounding rural countryside, typically within 4-10 hours travel time from the center city at prevailing wind velocities. Area III depicts rural or remote countryside greater than 10 hours travel time away from a city at prevailing wind velocities.

With the exception of atmospheric stagnations, highest daily maxima O_3 concentrations generally occur at sites in Area II. Maxima at Area I sites tend to be somewhat lower for several reasons. Ozone levels in this region are scavenged by fresh NO emissions which occur throughout the day. The O_3 accumulation process, described previously, takes several hours to reach its maximum. By that time, prevailing meteorological conditions have carried the relatively great emissions from Area I into Area II. Because there are fewer emissions in Area II, immediate scavenging by fresh sources of NO is reduced. By the time an urban plume typically reaches Area III, it is late in the day, further photolysis of NO_2 and certain other species is limited, and dilution and dry deposition result in a lowering of O_3 and its precursors.

FIGURE 2
CONCEPTUAL VIEW OF THREE AREAS EXPERIENCING IMPACTS FROM CONTROL STRATEGIES FOR OZONE


WIND
TRAVEL TIME
T=0
T=4 HR.
T=10 HR
AREA I
AREA II
AREA III

AREA I IS URBAN–CENTER CITY
AREA II IS SUBURBAN OR NEARBY RURAL
AREA III IS RURAL OR REMOTE

It is now appropriate to discuss the effect reducing VOC and NO_x emissions might have on ambient O_3 levels observed in Areas I and II. A discussion of Area III will be deferred until Section 3.0. The effect of controls can be assessed using models as well as a limited amount of trend data.

2.1 Implications from Photochemical Grid Model Strategy Runs

Application of photochemical grid models is particularly useful, because it most readily allows one to examine the impact of NO_x/VOC control strategies in Area I as well as in Area II. Results from a limited number of strategy runs involving both VOC and NO_x controls are available for Los Angeles (SCAQMD, 1982a), St. Louis (Cole, et al. 1982), the San Francisco Bay Area (ABAG, 1979, ABAG, 1982, Whitten, et al. 1981) and Denver (ABAG, 1979, Anderson, et al. 1977).

Four separate investigations have been conducted which include the impact of NO_x controls on predicted O_3 concentrations in the Los Angeles Basin (SCAQMD, 1981), (SCAQMD, 1982a), and (SCAQMD,1982b). Of these, a study conducted for the California Air Resources Board (SCAQMD, 1981) provides the most unambiguous assessment of the effects of NO_x control, so it will be discussed in greatest detail.

Table 1 is based on information obtained in the California Air Resources Board (CARB) study. In the CARB study, hypothetical control scenarios were applied uniformly throughout the basin. For example, if NMOC was reduced by 50% in Los Angeles County, it was also reduced by 50% throughout the rest of the Basin. As one can see from the Table, uniform NMOC reduction (columns (9) and (12)) is predicted to result in reductions in daily maximum O_3 at all locations in the Los Angeles Basin. In contrast, the predicted results of

TABLE 1

CHANGES IN PEAK OZONE MODELED IN SOUTH COAST AIR BASIN*

(1) Area	(2) Location	(3) Approx. Miles E. of Down-town LA	(4) Observed O_3, pphm	(5) Predicted Base Case O_3, pphm	(6) Strategy $\Delta HC = -75\%$ $\Delta NO_x = -75\%$	(7) $\Delta HC = -75\%$ $\Delta NO_x = -50\%$	(8) $\Delta HC = -75\%$, $\Delta NO_x = -25\%$	(9) $\Delta HC = -75\%$ $\Delta NO_x = 0$	(10) $\Delta HC = -50\%$ $\Delta NO_x = -50\%$	(11) $\Delta HC = -50\%$ $\Delta NO_x = -25\%$	(12) $\Delta HC = -50\%$ $\Delta NO_x = 0\%$	(13) $\Delta HC = 0$ $\Delta NO_x = -50\%$
I	Coastal (W.LA)	-12	<12-23.4	14.1	+15%	(-11%)	(-18%)	(-18%)	+2%	(-11%)	(-14%)	+26%
I	Central (DOLA, Anaheim)	0	13.5-25.0	20.1	(-1%)	(-17%)	(-29%)	(-31%)	(-1%)	(-14%)	(-26%)	+43%
II	S. Orange City (Costa) Mesa)	-	<12-28	13.5	(-28%)	(-14%)	(-12%)	(-17%)	(-12%)	(-7%)	(-11%)	(-4%)
II	San Gabriel Valley (Pasadena Azusa)	10	31.2-35.4	30.6	(-31%)+	(-25%)	(-35%)	(-41%)	(-11%)	(-20%)	(-30%)	0%+
II	Pomona Valley (Pomona, Upland)	30	26.5-49.1	35.6	(-43%)	(-29%)	(-31%)	(-38%)	(-23%)	(-20%)	(-25%)	(-17%)
II	SB/Riverside (Fontana, San Bernardino, Rubidoux)	50	21.8-47.6	38.0	(-47%)	(-30%)+	(-28%)+	(-32%)+	(-26%)+	(-18%)+	(-19%)+	(-22%)
Change in Basinwide Predicted Maximum		-		38.0	(-44%)	(-30%)	(-28%)	(-32%)	(-26%)	(-18%)	(-19%)	(-19%)

*Source: SCAQMD 1981
+Location of Predicted basinwide maximum

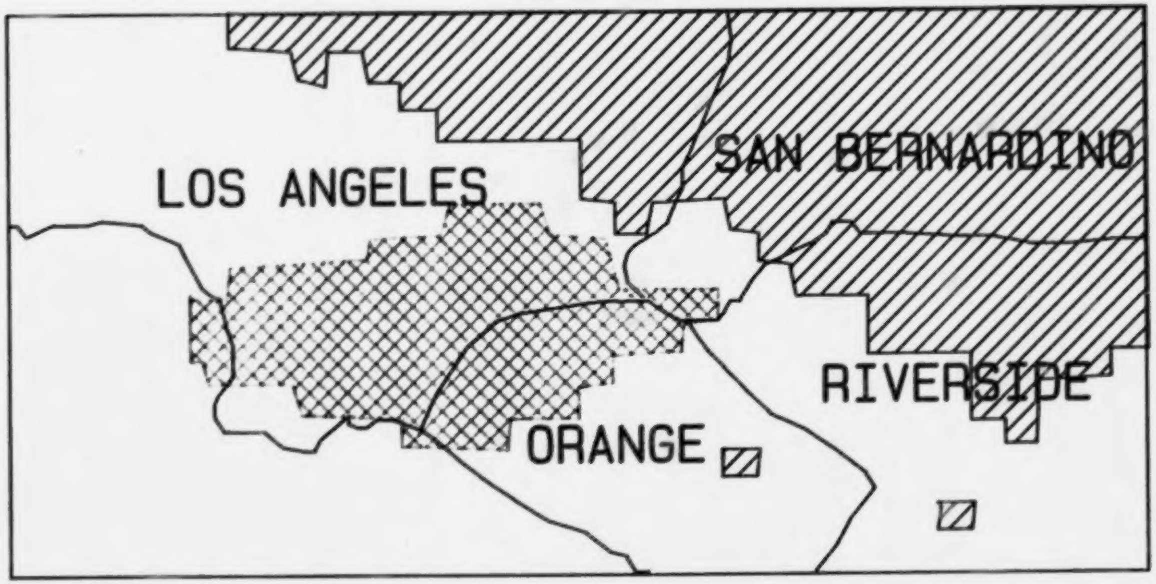
uniform NO_x reductions (column (13)) are mixed. In Area I (refer to Figure 2) locations, the CARB study suggests that reducing NO_x is counterproductive in reducing O_3. That is, for a given level of hydrocarbon control, the larger the reduction in NO_x, the smaller the reduction in O_3 (e.g., columns (6) - (9)). Reduction in NO_x alone leads to an increase in O_3 (column (13)). In Area II locations, moderate reductions in NO_x (i.e., up to about 50%) appear to lower the effectiveness of NMOC reductions (columns (7) - (12)). More drastic reductions in NO_x (i.e., column (6) vs. column (7)) lead to greater reductions in daily maximum O_3 levels for a given reduction in NMOC. Since highest O_3 levels prevail in Area II locations, a strategy calling for drastic reductions in NMOC and NO_x leads to the greatest reduction in the Basinwide daily maximum concentration of O_3 (column (6), last row).

The strategy simulations presented in Table 1 were obtained by using meteorological inputs believed appropriate for the second day of a 2-day episode (June 26-27, 1974). As a result, relatively high boundary conditions were assumed (e.g., NMOC = 0.216 ppmC, O_3 = .06 ppm). The use of high boundary conditions could affect the general applicability of the preceeding findings as well as explain some of the peculiar looking results (e.g., increase in O_3 at coastal sites accompanying 75% reductions in both NO_x and NMOC emissions). In addition, the results in Table 1 reflect emission levels and composition characteristics of the 1975-76 emission inventory for the South Coast Air Basin.

Examination of three other studies in the South Coast Air Basin suggests results which are, for the most part, qualitatively similar to those in the CARB study. First, a study sponsored by the SCAQMD (SCAQMD, 1982b) assumed lower boundary conditions (e.g., NMOC = .12 ppmC, O_3 = .04 ppm) and used a 1979 emissions inventory. Two strategies were examined. Strategy 1 assumed that VOC and NO_x emissions would be reduced to the forecast 1987 emissions (i.e., ΔNMOC = -33%, ΔNO_x = -23% from a 1979 base period). Strategy 2 added the effects of various additional controls which were regarded as feasible by 1987 by the SCAQMD (i.e., ΔNMOC = -49%, ΔNO_x = -37% from a 1979 base period).

Figure 3 is a "deficit diagram", which has been excerpted from the SCAQMD study (SCAQMD, 1982b). In the figure, cross hatched areas are those in which the daily maximum O_3 concentration at ground level increased as the result of applying the more stringent Strategy 2 instead of Strategy 1. Lined areas are those in which daily O_3 maxima decreased. Although the change in VOC emissions between the two strategies confounds the comparison somewhat, the results are essentially similar to the ones described earlier. That is, increased reductions in NO_x emissions (1) lead to increased O_3 levels near most major sources of NO_x and (2) result in lower concentrations of O_3 further downwind. Additional studies conducted separately by Systems Applications, Inc. (SAI) and studies sponsored by the Electric Power Research Institute (EPRI) yield qualitatively similar results in most respects (SCAQMD, 1982a). An exception is that the EPRI study does not indicate reductions in the basinwide daily maximum O_3 concentrations occurring whereas all of the

FIGURE 3. CHANGE IN MAXIMUM HOURLY OZONE CONCENTRATIONS IN SCAB IN 1987 RUN 1 MINUS RUN 2


LOS ANGELES
SAN BERNARDINO
RIVERSIDE
ORANGE

RUN 1: CHANGE IN VOC = -36%, NOX = -23%
RUN 2: CHANGE IN VOC = -49%, NOX = -37%

ADAPTED FROM SCAQMD (1982b)

other studies suggest that substantial reductions in NO_x will yield some reduction in the basinwide maximums (all of which are predicted to occur in downwind areas).

One further point merits discussion before we leave the Los Angeles modeling studies. As a rule, the majority of an urban area's population is likely to live near the area having the highest emissions of VOC and NO_x (i.e., Area I, Figure 2). Los Angeles is no exception to this rule. "Exposure" can be defined as the time period during which the population is exposed to a concentration above a specified level times the population exposed. Figure 4 depicts change in exposure accompanying SCAQMD Strategy 2 vs. Strategy 1 as a function of specified O_3 concentrations (SCAQMD, 1982b). We see in this example that if we specify a relatively low O_3 concentration (e.g., $\leq$ 15 pphm), the reductions in NO_x (and VOC) emissions actually lead to an increase in population exposure. This follows from the fact that a reduction of NO_x emissions of the magnitude associated with Strategy 2 leads to increases in the relatively low O_3 concentrations occurring near sources of NO_x, where most people in the Basin live. However, if our principal concern is to lower exposure to very high concentrations (e.g., greater than 15 pphm), this example indicates a decrease in exposure. The explanation for this latter finding is that such high O_3 concentrations are primarily found in downwind areas, and it is in these areas where the strategy ($\Delta HC=-49\%$, $\Delta NO_x=-37\%$) is most effective.

The Los Angeles modeling studies discussed in the preceding paragraphs are subject to an important caveat. This is that the studies do not allow us to infer the impact that NO_x control has on VOC control levels needed to

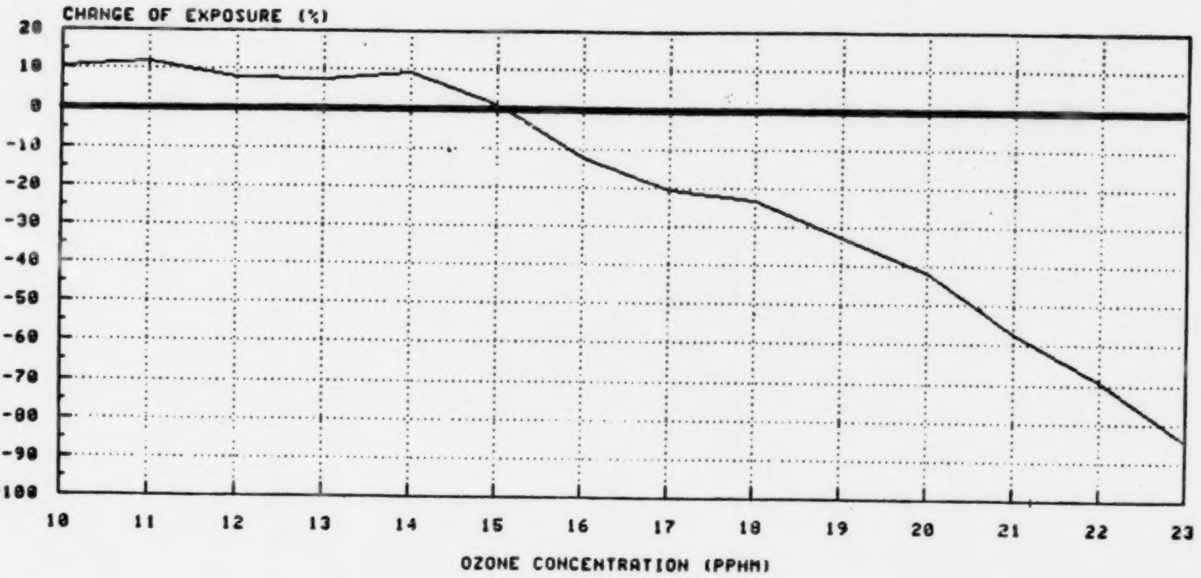


FIGURE 4.

CHANGES OF BASINWIDE TOTAL OZONE EXPOSURE FROM IMPLEMENTING STRATEGY 2 (ΔNMOC = -49%, ΔNO_x = -37%) vs. STRATEGY 1 (ΔNMOC = -36%, ΔNO_x = -23%).

Source: SCAQMD (1982b)

attain the O_3 NAAQS. It is this question which has been of greatest interest for regulatory applications. Also, the general applicability of the Los Angeles studies may be questioned because they were conducted for a limited sets of meteorological conditions and boundary conditions, and with a chemical mechanism which has since been updated. Further, prevailing concentrations of O_3 are much higher in Los Angeles than elsewhere. Grid Modeling studies conducted elsewhere are discussed in the next several paragraphs.

Several strategies involving NO_x controls have been simulated for St. Louis (Cole, et al. 1982). These studies utilize the 1975 emissions data base compiled for the RAPS study, assume low boundary conditions which are kept constant in the pre- and post-control simulations, and utilize meteorological data from 3 days on which high O_3 was observed to occur during 1976. The meteorological cases range from moderate wind flow (days 159, 195) to severe stagnation (day 275). The modeling domain considered in the St. Louis Study is smaller than that used in Los Angeles. That is, the maximum downwind distance (from Center City) for which O_3 is calculated is about 25 miles in St. Louis as opposed to about 75 miles for Los Angeles. Hence, we might expect that the predicted effect of NO_x controls would be less favorable in St. Louis than in Los Angeles, all other factors being equal.

The results of the St. Louis studies reported herein dwell on the impact of uniform reductions in NO_x emissions on the basinwide predicted maximum O_3 concentrations. The results of strategy runs for each of the three days simulated are shown in Figure 5. The negative slopes of the three lines in the figure indicate that, for the 42% level of NMOC control, reducing NO_x emissions results in higher peak O_3 than would occur if NO_x remained constant. We also note that on the day for which five strategies were simulated (Day

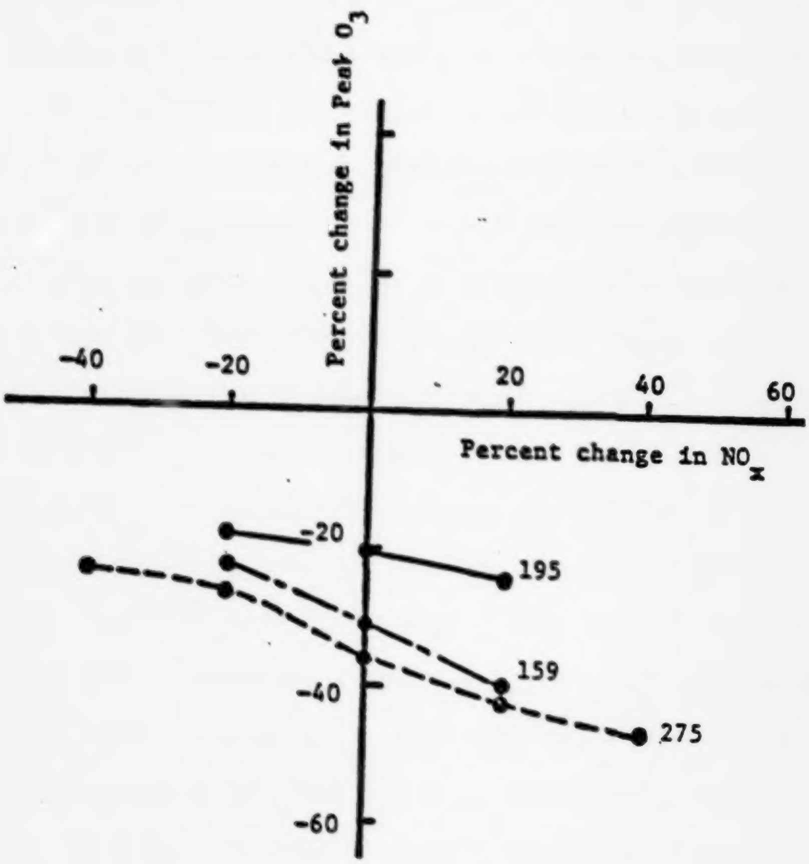


FIGURE 5. The effect of changes in NO_x emissions on the Airshed HC/O_3 response. Curves for three days generated using a 42% reduction in HC emissions.

Source: Cole, et al. (1982)

275), this slope reduces as changes in NO_x become more drastic. In the St. Louis studies, any benefits from NO_x control are less apparent than is the case for the Los Angeles results. This may be the result of the more limited modeling domain, somewhat lower NMOC/NO_x ratios derived from the RAPS data, as well as differing meteorological and boundary conditions.

The Association of Bay Area Governments (ABAG) has used the LIRAQ photochemical grid model (with LIRAQ2 chemistry) to assess the impact of NMOC and/or NO_x control on predicted O_3 concentrations in the San Francisco Bay area. Table 2 depicts change in basinwide peak hourly O_3 concentrations as a function of various strategies. ABAG (1982) also notes that NO_x control has an adverse effect on exposure to O_3 over the modeling domain (i.e., 100 km x 100 km). The results in Table 2 are qualitatively similar to those in Figure 5, and were obtained using a different grid model with a different chemical mechanism.

More limited assessments of NMOC and NO_x control are available for the Denver area as well (Anderson, et al. 1977 and ABAG, 1979). Here, the following strategies were compared: (1) a strategy reducing NMOC by 30%; (2) a strategy in which both NMOC and NO_x are reduced by 30%; and (3) a strategy in which NO_x was increased by 65%. It was found that the third strategy led to the greatest reductions in O_3 within the 30 mi x 30 mi modeling domain, whereas Strategy 2 resulted in the least reduction in O_3. It should be pointed out that the modeling domain in the Denver study is the smallest of those reviewed, and the chemistry used in the Urban Airshed Model (Carbon Bond I) is now dated. Nevertheless, the results are qualitatively similar to those obtained in San Francisco, St. Louis and Los Angeles.

TABLE 2.

SENSITIVITY OF PREDICTED PEAK OZONE IN THE BAY AREA TO VARIOUS CONTROL STRATEGIES

Results/Strategy									
	ΔHC(%)	0	-20	-40	-60	-80	-40	-80	0
	ΔNO_x(%)	0	0	0	0	0	-20	-40	-80
Predicted Peak O_3		.189	.140	.082	.069	.055	.119	.064	.233
% Change in Peak O_3		-	-26%	-57%	-63%	-71%	-37%	-66%	+23%

Source: Whitten, et al., 1981

2.2 Implications from EKMA

In Section 2.0, we noted that presence of both NMOC and NO_x is necessary for high concentrations of O_3 to be formed. It follows that if the amount of NMOC is great in relation to the available NO_x, the formation of O_3 will be limited by the available NO_x, and vice versa. This relationship is usually expressed quantitatively using the NMOC/NO_x ratio which occurs in the morning before the onset of photochemistry.

Relative amounts of NMOC and NO_x are considered implicitly in the previously described photochemical grid modeling studies. For example, a review of extensive NMOC and NO_x data collected during the RAPS study suggests that the prevailing NMOC/NO_x ratio in St. Louis during 1976 was about 8:1 (Freas, et al. 1978). More recent measurements made during summer 1985 suggest typical ratios in St. Louis in the order of 9-10:1. Although there is considerable uncertainty over what NMOC/NO_x ratios exist in Los Angeles, the South Coast Air Quality Management District used ratios ranging from 9-11:1 as best estimates in a 1982 EKMA analysis for the South Coast Air Basin (SCAQMD, 1982c). Los Angeles, St. Louis, San Francisco and Denver are large cities with diverse mixtures of sources. Gipson (1984a,b) has reviewed NMOC species data measured in large cities in the Northeast Corridor with diverse mixtures of sources. This review suggests that the reactivity of the organic species mix is similar in each of these cities, and can be characterized reasonably well by a default mixture recommended by Killus, et al. (1984). Finally, all four cities had severe O_3 problems (Max. $O_3 > .18$ ppm) during the periods modeled with the grid models. Hence, the results reported in Section 2.1 are probably most applicable for large cities with diverse sources of precursors, severe O_3 problems and prevailing NMOC/NO_x ratios in the order of 7-12:1.

What can be said about cities having less severe O_3 problems, differing $NMOC/NO_x$ ratios and/or mixes of organic pollutants with differing reactivities? In this section, the EKMA model is used to address these questions.

Figure 6 is an example of an O_3 isopleth diagram of the sort generated by the OZIPM model underlying EKMA (Gipson, 1984c). In these diagrams, maximum hourly O_3 is plotted as an explicit function of initial NMOC and NO_x precursor concentrations, and as an implicit function of reactivity, meteorological assumptions, boundary conditions and diurnal emission patterns. The solid diagonal line in Figure 6 is a line of constant slope, and depicts an $NMOC/NO_x$ ratio. The dashed lines represent high and low $NMOC/NO_x$ ratios. If we examine the "high ratio" line, we find that the shape of the isopleth diagram is such that reducing NO_x levels will produce more apparent benefit than reducing NMOC. Conversely, the "low ratio" line implies greater benefits from reducing NMOC.

Isopleth diagrams like Figure 6 can be used to gain insight into the relative efficacy of reducing NMOC vs. reducing NO_x under various conditions. To gain such insight we define the "Equal Control Ratio" (ECR).

The ECR is defined as that $NMOC/NO_x$ ratio at which equal relative reductions in NMOC or in NO_x would result in attainment of the NAAQS for O_3. The ECR is illustrated conceptually in Figure 7 for an observed O_3 concentration of 0.24 ppm and for the set of assumptions used to generate the diagram in Figure 7. Interpretation of Figure 7 is relatively straightforward. In the example shown, for $NMOC/NO_x$ ratios which are greater than (i.e., to the right and below) the ECR would require less relative reduction in NO_x than in NMOC to meet the NAAQS for O_3. That is,

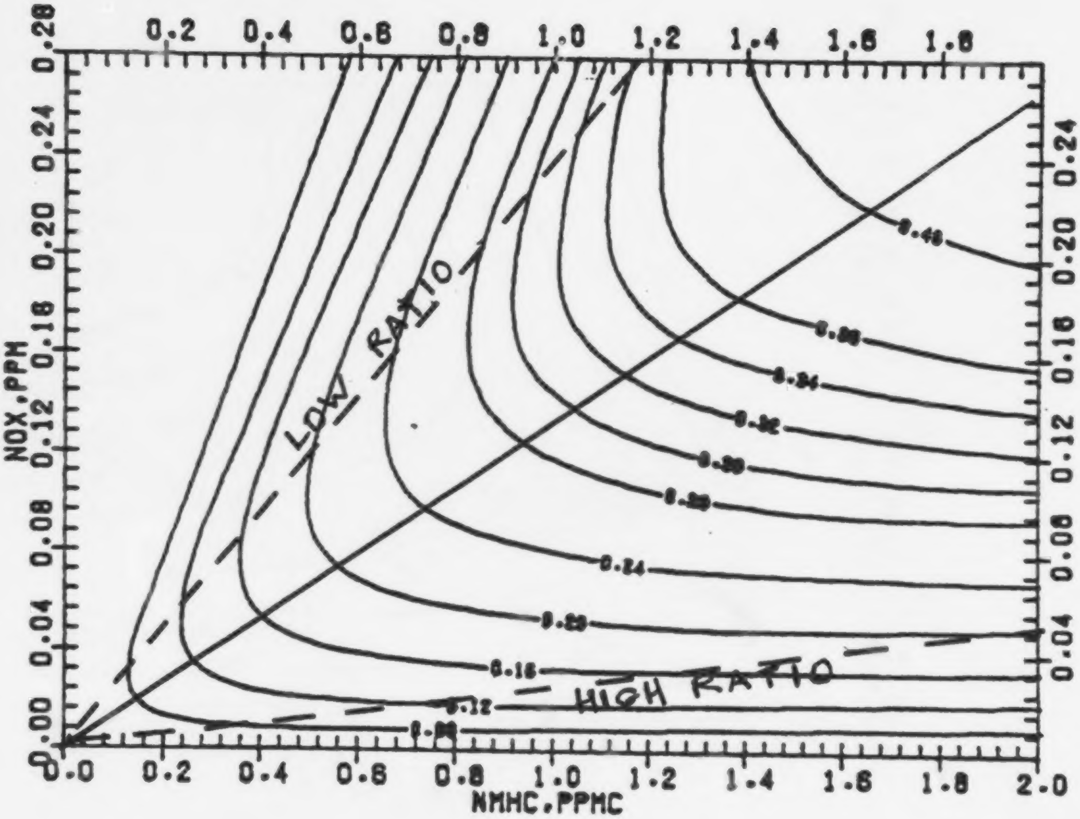


FIGURE 6. Example Ozone Isopleth Diagram

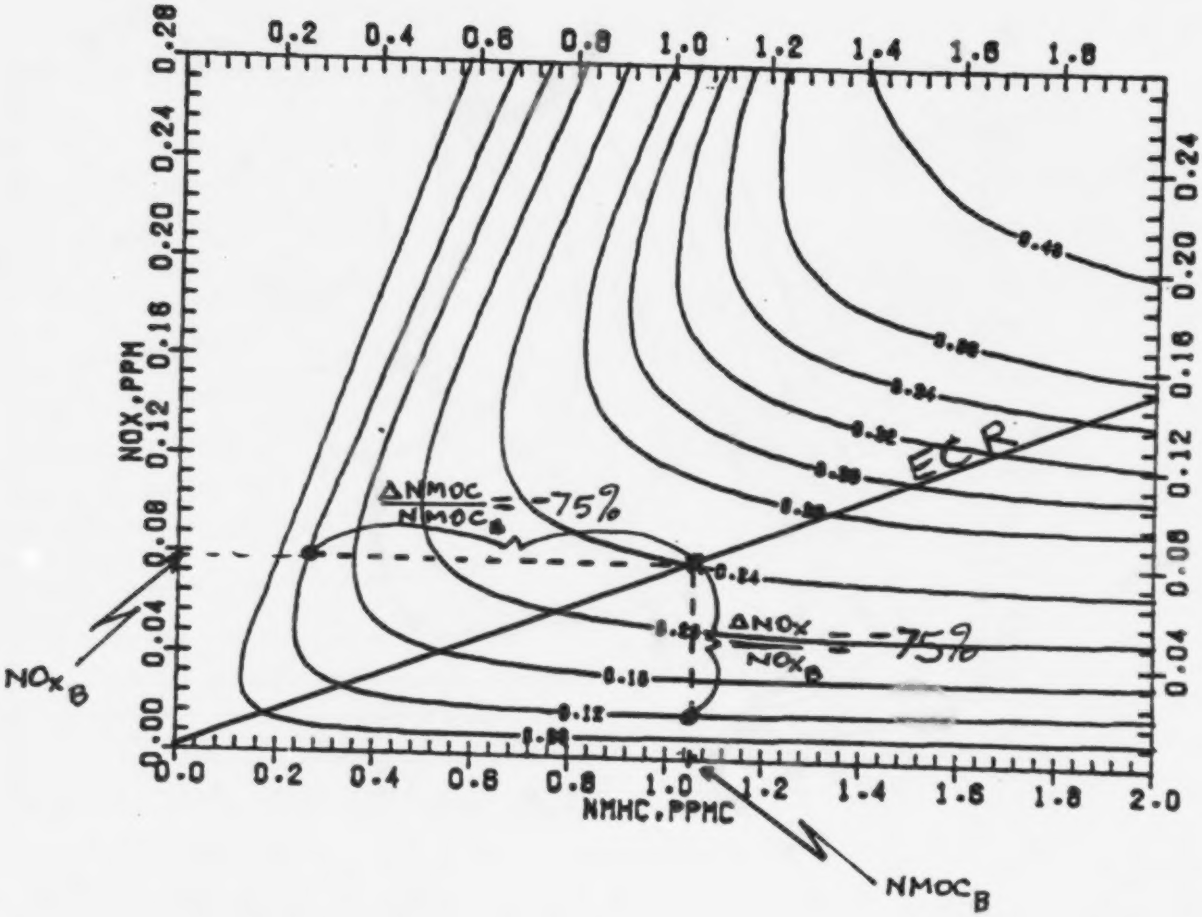


FIGURE 7. Concept Underlying "Equal Control Ratio"

$$\frac{\Delta NO_x}{NO_{xB}} < \frac{\Delta NMOC}{NMOC_B} .$$

The shape and spacing of an isopleth diagram depends on a number of the implicit meteorological, air quality and emission assumptions identified previously. Therefore, one might expect that the value of the ECR depends on these assumptions as well. To test this hypothesis, we have conducted a series of sensitivity studies using EKMA with the Carbon Bond 3 (CB-3) chemical mechanism. In these studies, recommended default values were assumed for boundary conditions and diurnal emission patterns (Gipson, et al. 1983 and Gipson, 1984d). Effects of reactivity, atmospheric dilution and severity of an areas's O_3 problem on the ECR were assessed. Table 3(a) summarizes the results for "pure" (i.e., VOC reduction only or NO_x reduction only) VOC and NO_x strategies. In Table 3(a), "high", "default" and "low" reactivities correspond to three different NMOC mixtures investigated by Gipson (1984b). "Low", "Medium" and "High" dilution are identified in Gipson, et al. 1983.

We see from Table 3(a), that the ECR increases with decreasing reactivity, with increasing severity of the O_3 problem and with increasing dilution. The "default" reactivities underlying the results in Table 3 were recommended by Killus, et al. (1984), and are based on empirical observations in a number of cities. Further, as previously noted, Gipson (1984a) has found that the default mix adequately describes reactivity in additional cities. Therefore, if we assume that the "default reactivity" adequately characterizes the NMOC mix in most cities, we conclude that the ECR for "pure" VOC vs. "pure" NO_x strategies is probably between 10-20:1 over a range of O_3 severity and dilution conditions encompassing most cities in the U.S. having problems attaining the O_3 NAAQS.

TABLE 3.

BASE LEVEL NMOC/NO_x RATIOS LEADING TO EQUAL NMOC AND NO_x CONTROLS NEEDED TO ATTAIN THE OZONE NAAQS

(a) NMOC-Only vs. NO_x-Only Strategies

Scenario	Base Level O_3	0.16		0.20		0.24	
		Equal Control Ratio	% Control	Equal Control Ratio	% Control	Equal Control Ratio	% Control
Low Dilution	High Reactivity	4.5:1	65%	6.3:1	76%	7.5:1	79%
	Default Reactivity	12:1	72%	12:1	72%	14:1	77%
	Low Reactivity	9:1	68%	12:1	76%	16:1	80%
Medium Dilution	High Reactivity	6:1	58%	7:1	72%	9:1	77%
	Default Reactivity	11:1	70%	12:1	70%	15:1	75%
	Low Reactivity	12:1	55%	17:1	68%	22:1	73%
High Dilution	High Reactivity	7:1	65%	8:1	75%	10:1	82%
	Default Reactivity	10:1	65%	16:1	75%	20:1	82%
	Low Reactivity	16:1	60%	22:1	75%	26:1	78%

(b) NMOC-Only vs. Identical NMOC and NO_x Reductions

Medium Dilution	Default Reactivity	7.5:1	56%	10:1	67%	15:1	75%

Table 3(b) compares a "pure" VOC reduction strategy vs. a strategy calling for equal percent reductions in VOC and NO_x. Here we see that the ECR for these two types of strategies tends to be lower than is the case when a "pure" VOC strategy is compared with a "pure" NO_x strategy. Thus, for the example shown, Table 3(b) indicates that if the base level O_3 concentration is 0.20 ppm and the NMOC/NO_x ratio is greater than 10:1, a smaller percent reduction in VOC is needed to attain the NAAQS if NO_x is reduced by a comparable percentage than would be the case for a "pure" VOC strategy.

While the ECR is a useful concept, it does not take account of cost and/or technological feasibility of VOC vs. NO_x controls. In reality, these latter factors may be of overwhelming importance in selecting an appropriate control strategy for a city. To illustrate the potential importance of control cost/technical feasibility factors, we introduce a new term: the "equal control cost ratio" or ECCR. The ECCR is defined as that NMOC/NO_x ratio at which the cost of reducing NMOC to attain the O_3 NAAQS equals that of reducing NO_x. Borrowing an example from Bilger (1978), to illustrate, suppose for the situation exemplified by Figure 7, it cost twice as much to reduce NO_x as it does to reduce NMOC by the same relative amount. This would mean that it would be more economical to control NMOC unless the NMOC/NO_x ratio were such that:

$$\frac{\Delta NMOC}{NMOC_B} \geq (2) \frac{\Delta NO_x}{NO_{xB}}$$

Using this example, the ECCR is illustrated further in Figure 8, assessing a peak observed O_3 concentration of 0.20 ppm.

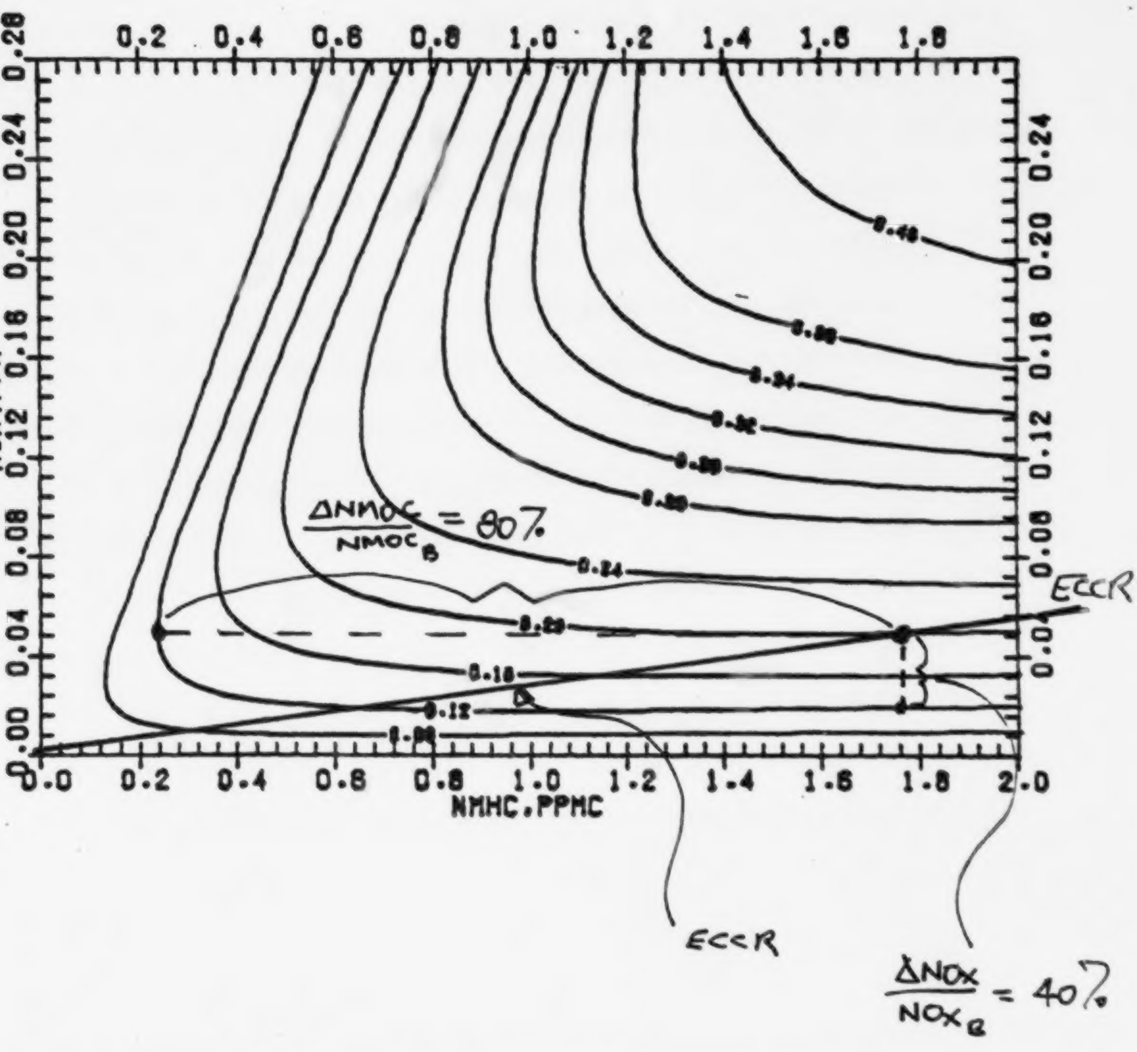


FIGURE 8. Concept Underlying "Equal Control Cost Ratio"

Clearly, a strategy requiring control of both VOC and NO_x would be more costly than one calling for VOC reductions only. In the preceding example, a "pure" VOC strategy would be preferred unless

$$\left[\frac{\Delta NMOC}{(NMOC)_{initial}}\right]_{pure} \geq \left[\frac{\Delta NMOC}{(NMOC)_{initial}} + (2)\,\frac{\Delta NO_x}{(NO_x)_{initial}}\right]$$

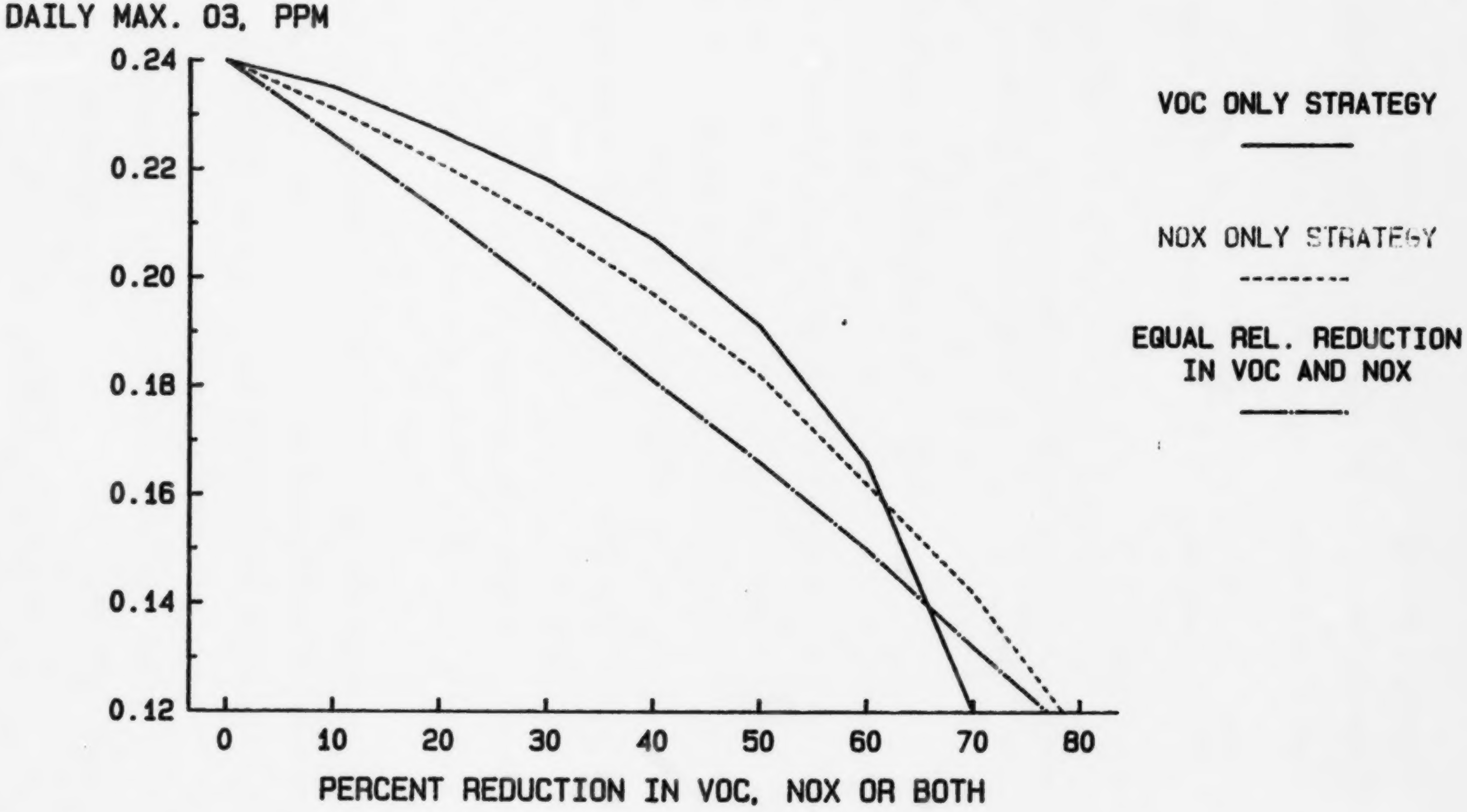
or, more generally,

$$\text{cost}\left(\begin{array}{l}\text{Pure NMOC}\\ \text{attainment}\\ \text{strategy}\end{array}\right) \geq \text{cost}\left(\begin{array}{l}\text{attainment strategy involving}\\ \text{reductions in VOC and } NO_x\end{array}\right)$$

The ECCR would be expected to exhibit sensitivities to reactivity, dilution and O_3 severity which are in the same direction as those affecting the ECR. However, it is much more difficult to make general estimates of the ECCR, because it requires knowing cost vs. control functions for each source category of VOC and NO_x as well as a knowledge of the mix of VOC and NO_x sources within a city. As Bilger (1978) notes however, there is a general perception that large amounts of VOC control are less costly and more feasible than large amounts of NO_x control. If this is true, we are probably safe in assuming that, for "pure" VOC and "pure" NO_x strategies, the ECR represents a lower estimate for the ECCR in urban areas subject to O_3 levels well above the NAAQS.

In choosing a strategy to reduce O_3 in and downwind from urban areas, it may be useful to consider how rapidly one might expect any reduction in O_3 to occur. Grid models or EKMA can be used to provide insight into this issue. Figure 9 was obtained using EKMA/CB3 with boundary conditions, emission patterns, default reactivity and medium dilution as defined in several reports by Gipson (1983, 1984b, 1984d). The curves in Figure 9 depict daily maximum

FIGURE 9
DAILY MAXIMUM OZONE AS A FUNCTION
OF APPLIED CONTROLS



NMOC/NOX RATIO = 12:1
RESULTS OBTAINED WITH EKMA/CB3, RIA2 ASSUMPTIONS

O_3 as a function of relative reductions in VOC, NO_x or both precursors, given a base level O_3 concentration of 0.24 ppm and an initial NMOC/NO_x ratio of 12:1. Since, under the assumed conditions, an NMOC/NO_x ratio of 12:1 is less than the ECR (15:1) shown in Tables 3(a) and (b), percent reduction in VOC needed to attain the NAAQS in a "pure" VOC strategy is less than relative reductions of NO_x or VOC and NO_x in the other strategies. However, for the conditions simulated, we also see that large reductions in VOC are necessary before a "pure" VOC strategy becomes as effective as the others in reducing O_3.

Before we leave this Section, it is necessary to remind the reader that the conclusions/illustrations obtained with EKMA may depend on the input assumptions to the model as well as the starting point on the EKMA diagram. Although the results reported herein will be used, together with other types of analyses, to draw some general conclusions regarding strategies in subsequent Sections, city-specific case-by-case analyses are recommended.

2.3 Implications From Trend Analyses

It is next appropriate to examine available air quality and emission trend data to determine the extent to which effects of controlling NO_x and VOC predicted by models have been borne out by actual experience. Although many urban areas have ongoing regulatory programs to reduce O_3, the most extensive and reliable records are available for the South Coast Air Basin. Since this is also the region where the most extensive modeling of NO_x control strategies has been performed, our review of trend information will be confined to this area.

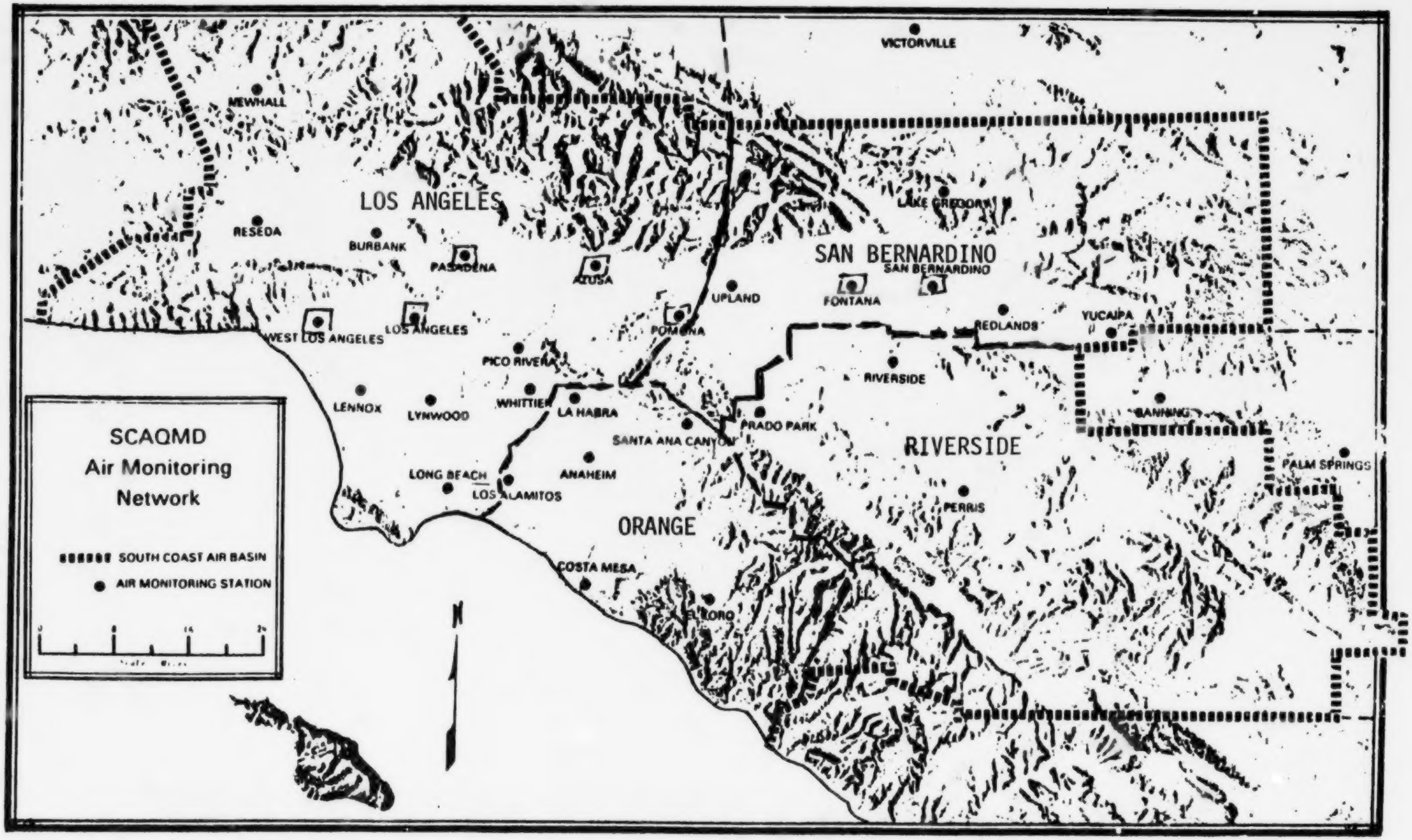
Trend data are difficult to interpret, because they are subject to a number of confounding factors such as annual fluctuations in meteorology, growth patterns which are not uniform, changes in air quality instrumentation/

procedures, potential differences in a monitor's microscale environment and possible differences in emission inventory techniques over a long period of historical record. In addition, there may be considerable uncertainty over key factors such as historic emission inventories and NMOC/NO_x ratios. In particular, ratios of VOC to NO_x emissions often differ from measured ambient ratios. There are few ambient NMOC data available against which to compare emission trends. Therefore, the best we can hope to do is to examine available trend data to see whether they provide qualitative agreement with what we have been able to conclude so far about the relative effects of reducing NMOC and/or NO_x.

Figure 10 indicates the location of the four counties comprising the South Coast Air Basin (SCAB), and the location of key monitoring sites used in the subsequent analyses (SCAQMD, 1982d). Figure 11 plots yearly maximum O_3 concentration averaged over 3 years. For example, values shown for 1965 are the average of yearly maxima observed at a particular site during 1964, 1965 and 1966. Averaging yearly maxima in such a way is intended to reduce confounding factors introduced by varying meteorology. Data from each of the 7 sites considered are plotted in such a way that their horizontal position is roughly proportional to their distance from downtown Los Angeles, so as to provide a rough view of O_3 levels along the prevailing wind direction. To show trends in the spatial distribution of O_3, the process used in plotting the curve for 1965 was repeated at 5 year intervals for 1970, 1975 and 1980. We see from Figure 11 that there was a marked improvement in the trend parameter for West Los Angeles and for downtown Los Angeles between 1965 and 1970, with little improvement thereafter. Further downwind, we note relatively little change in O_3 at Pasadena, Azusa and Pomona between 1965-70,

FIGURE 10.

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT AIR MONITORING STATION LOCATIONS

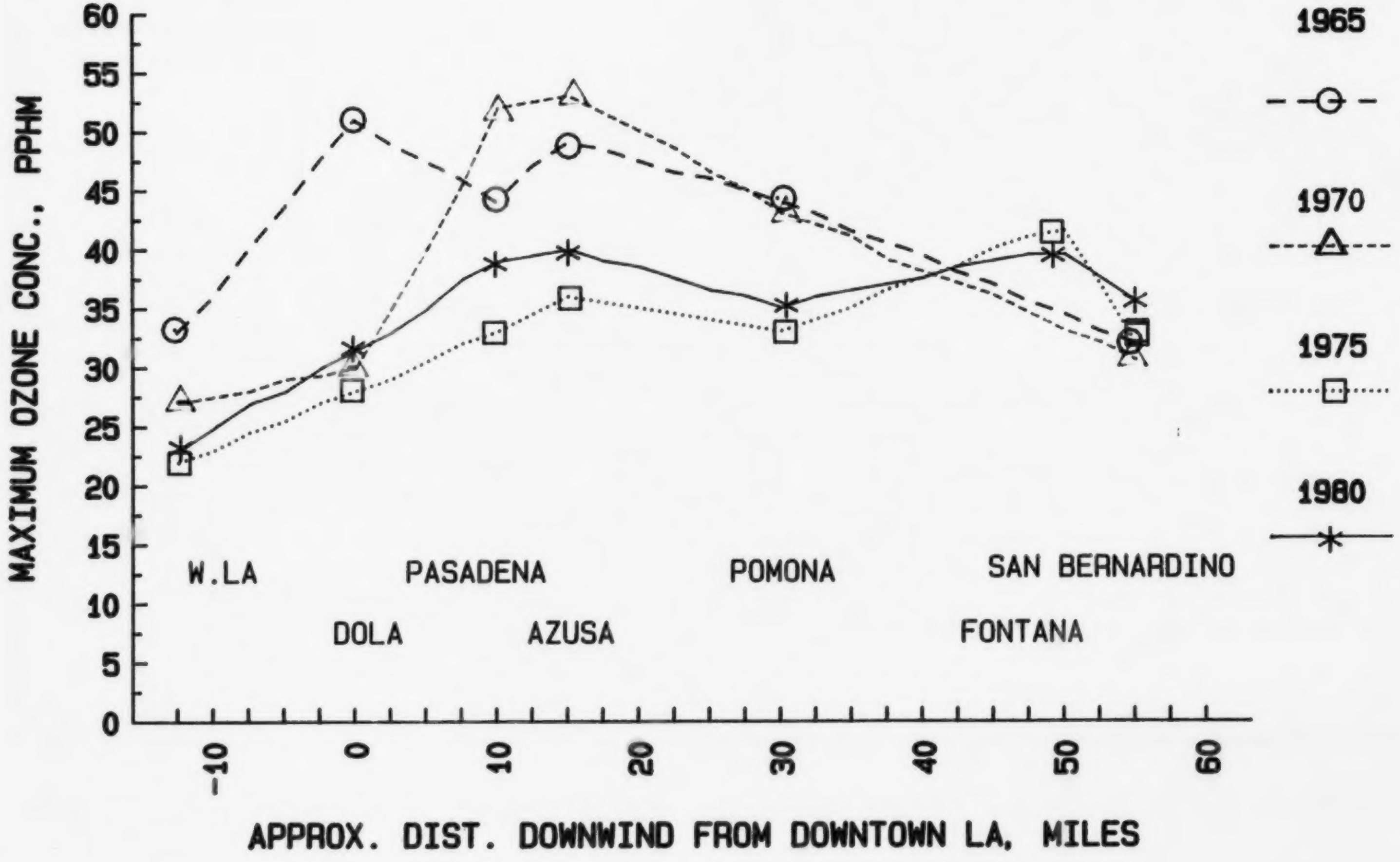

VICTORVILLE
NEWHALL
LOS ANGELES
RESEDA
BURBANK
PASADENA
AZUSA
LAKE GREGORY
SAN BERNARDINO
SAN BERNARDINO
UPLAND
FONTANA
POMONA
REDLANDS
YUCAIPA
WEST LOS ANGELES
LOS ANGELES
PICO RIVERA
RIVERSIDE
LENNOX
LYNWOOD
WHITTIER
LA HABRA
PRADO PARK
BANNING
SANTA ANA CANYON
RIVERSIDE
PALM SPRINGS
LONG BEACH
LOS ALAMITOS
ANAHEIM
PERRIS
ORANGE
COSTA MESA
EL TORO
N
SCAQMD
Air Monitoring
Network
SOUTH COAST AIR BASIN
AIR MONITORING STATION

The Upland station is operated by the California Air Resources Board. Victorville is operated by San Bernardino County APCD.

☐ Sites plotted on Figure 11

Reproduced from
best available copy.

FIGURE 11
TREND IN SPATIAL PATTERN OF 3-YEAR
AVERAGE YEARLY MAXIMUM OZONE IN LA BASIN



marked improvement between 1970-75 and relatively little change thereafter.* At the farthest downwind site (San Bernardino) we note a slightly increasing trend in O_3 between 1965 and 1980.

In order to provide a possible explanation for the observations in Figure 11, it is necessary to review demographic and emissions trends in the South Coast Air Basin. Between 1960 and 1980, the population of the four counties comprising SCAB has increased about 25%. However, the most dramatic growth has occurred in Orange, Riverside and San Bernardino counties. In 1960, the population in Los Angeles County was about 4 times that of the other three counties combined. In 1980, population in these other three counties totals about half that in Los Angeles County. Hence, there has been disproportionately large growth in population (and emissions) further east (i.e, downwind). Nevertheless, Los Angeles County emissions are still, by far, the greatest in the Basin (CARB (1986)).

In Figure 12 we see that Basinwide emissions of VOC have been decreasing fairly steadily between 1966 and 1984. In contrast, NO_x emissions increased from the mid '60's to about 1978 and have decreased thereafter at a slightly greater relative rate than the VOC reductions.

In terms of air quality trends in the Basin, we see that there are essentially 2 periods of note: 1965-1975, where there was a pronounced decrease in maximum O_3 in Los Angeles County as well as basinwide, and 1975-80 where there is little change. During the former period VOC emissions decreased by about 12% while NO_x increased about 19%, leading to an estimated 26%

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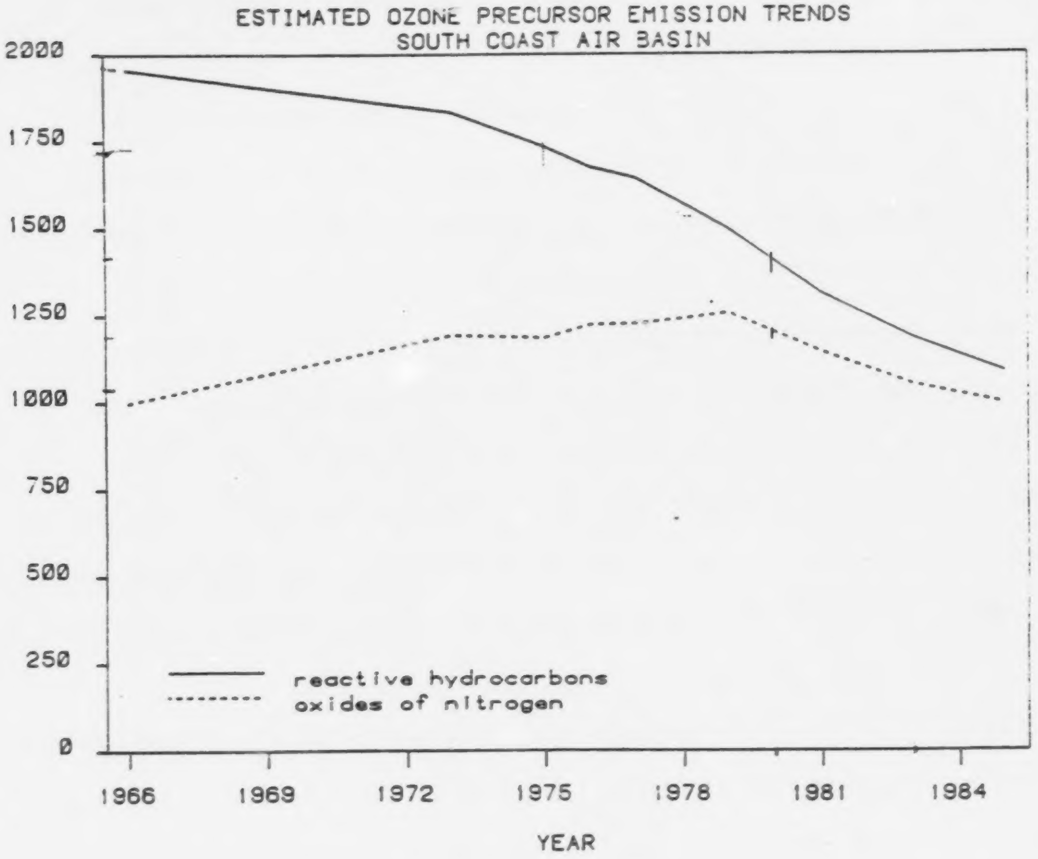
*A recent CARB report (CARB 1986) has cautioned that the reduction in average daily maximum O_3 at these sites during 1970-75 may, for unknown reasons, be overstated.

FIGURE 12

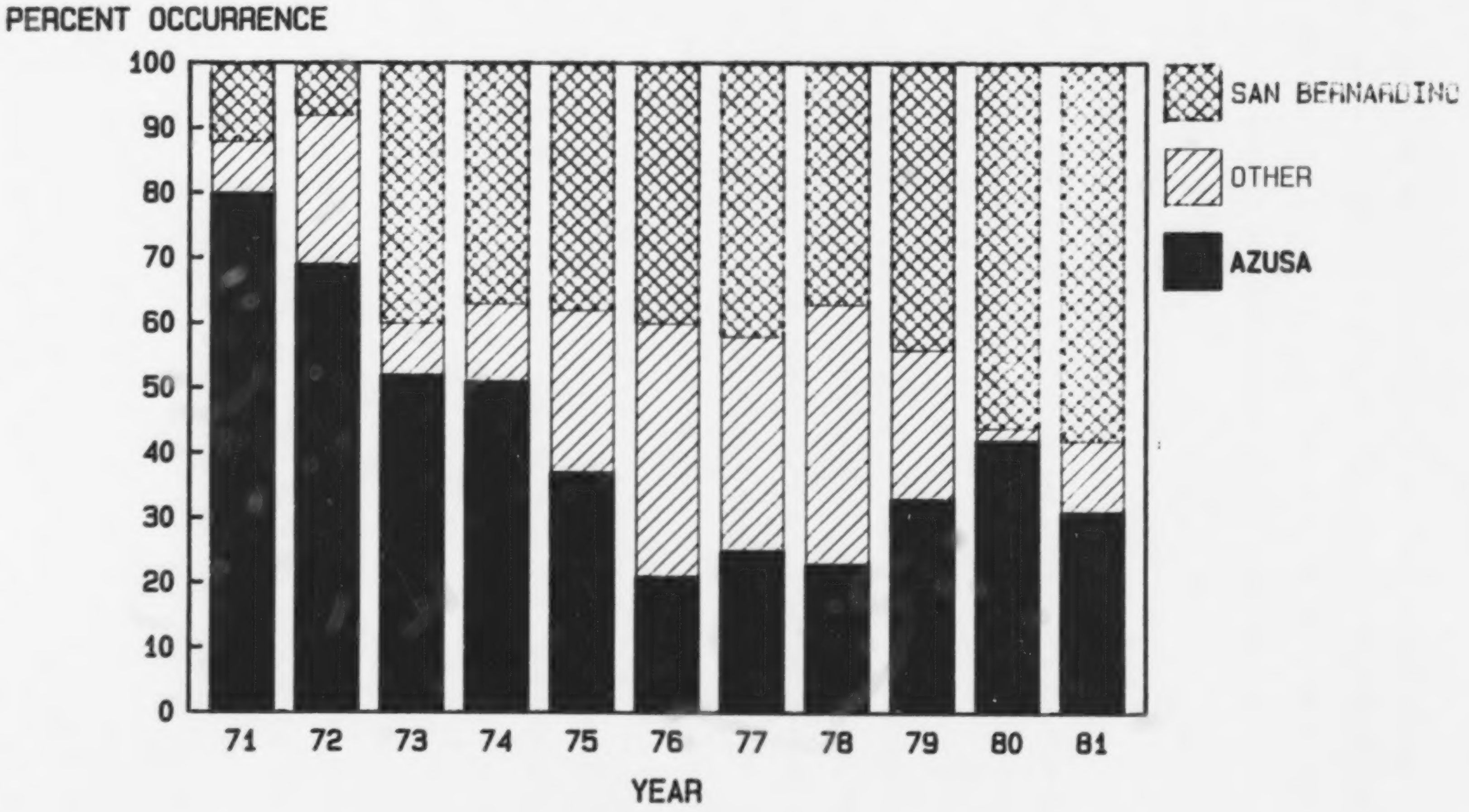


SOURCE: CARB (1986)

decrease in the ratio of VOC to NO_x emissions. One would expect to see a moderate decrease in maximum O_3 within a county having ambient $NMOC/NO_x$ ratios in the order of 10:1. We see from Figure 11 that between 1965-1980 Basinwide maximums were reduced by about 21% and Los Angeles countywide maximums were reduced by about 32%. This reduction is somewhat greater than implied from Airshed Modeling results where (1) SCAQMD (1981) estimated a 19% reduction in the Basinwide maxima and a 25% reduction in the countywide maxima accompanying a 50% reduction in the VOC/NO_x emissions ratio (i.e., $\Delta NMOC = -50\%$, $\Delta NO_x=0$) and (2) Cole et al. (1982) estimated a 20-35% decrease of ozone maxima accompanying a 42% reduction in the ratio in the smaller modeling domain at St. Louis. However, CARB (1986) has cautioned that the apparent reduction in observed peak O_3 may be overstated.

During the latter period (1975-80), VOC emissions were reduced by about 17%, NO_x was about constant and the resulting ratio of VOC to NO_x emissions decreased by about 17%. During 1975-80, we observe a small (~5%) decrease in the Basinwide maximum but an 11% increase in the Los Angeles County maximum. The basinwide maximum during this latter period appears to have shifted further downwind, but the trend in its value is small. A recent analysis of Los Angeles trends by Kumar, et al. (1984) also notes a downwind shift in Basinwide maxima as a result of the long-term strategy of emphasizing VOC controls. Figure 13 is reproduced from this latter study. This figure depicts the relative frequency with which the Basinwide daily maximum O_3 concentration occurs far downwind (San Bernandino) vs. closer to downtown Los Angeles (Azusa). We note an increase in the percentage of Basinwide daily maxima occurring further downwind, (at San Bernardino) between 1971-81 with a corresponding decrease at

FIGURE 13
FREQUENCY OF MAXIMUM OZONE AT VARIOUS SITES



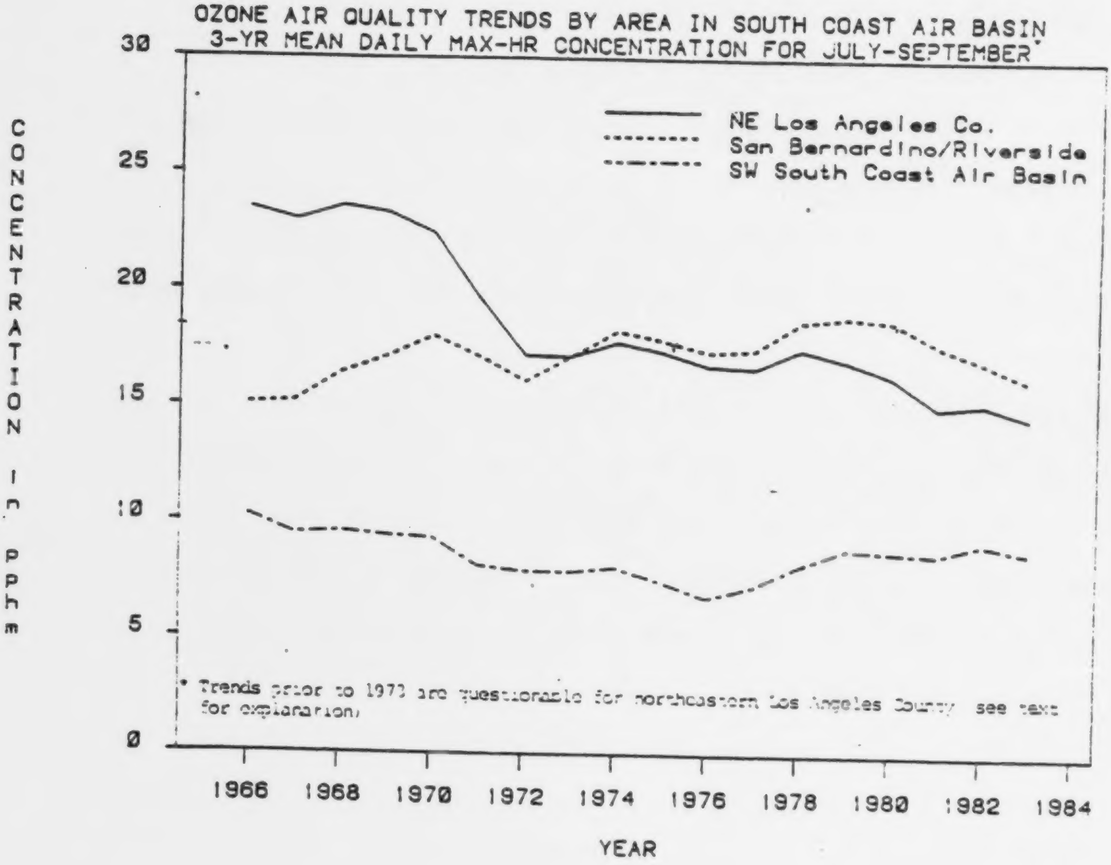
Azusa. Thus, the observed shifts in the magnitude and location of observed peak O_3 levels are in qualitative agreement with model predictions.

In a recent report (CARB (1986)), CARB has reviewed the effect of the more vigorous NO_x control program begun in the late 1970's on O_3 trends observed in the South Coast Air Basin between 1978-1983. Figure 14 is excerpted from that report. Figure 14 uses a more robust trend parameter (mean daily maximum O_3 concentration) than shown in Figure 11. Further, the trends shown have been spatially averaged for a number of sites. Nevertheless, trends shown in Figures 11 and 14 are similar. Both figures show a pronounced decrease in Basinwide O_3 maximum between 1965-75, with little change between 1975-80. Both figures show a shift in the Basinwide maximum further downwind. However, between 1978-83, Figure 14 shows a decrease in both Basinwide and Los Angeles County maximas. In addition there is a small increase in O_3 in the western (upwind) part of the Basin. CARB attributes the foregoing observations to the more vigorous NO_x reduction programs which began to accompany the VOC control program in the late 1970's. The more limited amount of the O_3 increase in the NO_x source-intensive area than that anticipated from modeling results may be due to an emphasis on NO_x controls from elevated sources.

2.4 Summary

Modeling and trend information have been reviewed to estimate effects of controlling NO_x and NMOC on daily maximum O_3 concentrations within one day's travel time of a city. Our findings suggest that if the prevailing NMOC/NO_x ratio is less than about 10:1 and the reactivity of a city's NMOC mix is typical, VOC controls are the most effective means for attaining the NAAQS for O_3. For cities in which NMOC/NO_x ratios are about 10:1 or greater, the

FIGURE 14



OZONE AIR QUALITY TRENDS BY AREA IN SOUTH COAST AIR BASIN
3-YR MEAN DAILY MAX-HR CONCENTRATION FOR JULY-SEPTEMBER*

* Trends prior to 1973 are questionable for northeastern Los Angeles County see text for explanation)

SOURCE: CARB (1986)

picture is less clear. The most effective strategy (VOC, NO_x or reductions in both) depends on a number of factors including severity of the O_3 levels, reactivity, dilution and cost. Generally, the Equal Control Ratio (ECR) increases with increasing severity of the O_3 problem, decreasing reactivity and increasing atmospheric dilution. Because cost information is likely to depend on a city-specific mix of sources and because of the other factors mentioned above, case-specific evaluations of VOC vs. NO_x strategies would be necessary to determine the most appropriate strategy.

Modeling results from locations having NMOC/NO_x ratios in the order of 10:1 suggest the following:

(a) Controlling NO_x may increase O_3 levels near sources of NO, unless VOC emissions are reduced substantially (see Table 1). This undesirable feature of NO_x control can perhaps be reduced by emphasizing control on elevated sources.

(b) In areas up to about 20-30 miles downwind of NO_x source-intensive locations subject to severe (e.g., $\geq$ 0.18 ppm) O_3 levels, moderate reductions in NO_x (e.g., ~25%) may reduce effectiveness of VOC reduction strategies; benefits in these areas appear only after drastic curtailment of NO_x;

(c) Because of the distribution of urban populations, in areas subject to very high O_3 concentrations (e.g., Los Angeles), exposure to concentrations of O_3 above the level of the NAAQS (e.g., ~0.12ppm) may increase as the result of vigorous strategies to reduce NO_x; however, exposure to higher concentrations (e.g., $\geq$ 0.16 ppm) may decrease.

(d) In contrast, VOC control appears to be uniformly beneficial with greatest benefits occurring near locations where NO_x levels are relatively high;

(e) In areas subject to severe O_3 concentrations (e.g., $\geq$ 0.18 ppm), moderate control of both VOC and NO_x ordinarily appears to be less effective in reducing daily maximum levels of O_3 within 20-30 miles of NO_x source-intensive areas than are strategies to control VOC alone by moderate to drastic amounts. However, controlling both VOC and NO_x may be more effective in reducing O_3 (sometimes the peak areawide O_3) further downwind (e.g., $> \sim 30$ miles) than is controlling VOC only.

(f) Areas subject to less severe ($\leq$ 0.17 ppm) O_3 may sometimes be able to meet NAAQS more readily by reducing both VOC and NO_x. A case-by-case modeling analysis is necessary to prescribe the most effective strategy.

(g) Under some conditions, reductions in peak O_3 may occur most rapidly if both VOC and NO_x are reduced. However in some cases, controlling NO_x may increase the amount of VOC control ultimately needed to attain the NAAQS.

Air quality trend data from Los Angeles appear reasonably consistent (although not entirely so) with modeling results. During a period (1965-75) in which VOC emissions decreased and NO_x emissions increased (resulting in a moderate decrease in VOC/NO_x emission ratio), we see some reduction in the Basinwide daily maximum O_3 and an even greater decrease at sites nearer to the major area of precursor emissions. During a second period (1975-80), in which NO_x emissions were about constant and reduction in the VOC/NO_x ratio was smaller, smaller changes in O_3 were observed. During a third period (1978-83) where NO_x reductions accompanied VOC reductions, the O_3 trend far downwind reverses and begins to decrease. In addition, there is a small increase in O_3 near source-intensive areas. Finally, the Los Angeles trend data suggest that one net effect of control programs (where selective reduction in VOC has been greater than for NO_x) has been to shift the Basinwide peak O_3 further downwind in addition to reducing the severity of the concentrations.

The reader should be cautioned once again that our review is based on analysis of relatively few locations using a limited number of modeling/chemical assumptions. A case-by-case review is urged for specific regulatory applications. Nevertheless, the results which are obtained appear, on the whole, to be consistent with one another.

3.0 Ozone Concentrations In Rural Or Remote Areas

We now turn to the implications of NO_x and VOC control on O_3 observed in rural/remote locations greater than a single day's (e.g., 10-hours) travel time downwind from urban areas at prevailing wind velocities. Unlike the "single day" problem discussed in Section 2, models to quantify effects of controls on multiday or rural O_3 levels are still under development. Hence, judgments concerning the effects of controls must be based on more qualitative information. Several years ago, the Office of Air Quality Planning and Standards (OAQPS) asked the Atmospheric Sciences Research Laboratory (ASRL) to prepare a "state of the science" assessment concerning the role of NO_x in rural O_3 formation. The resulting effort has led to a review and assessment by Altshuller (1986). Much of the information presented in this section is based on material contained in this report. An additional earlier review conducted for OAOPS (Martinez et al. 1979) has also been used liberally.

Four hypotheses can be advanced to explain high concentrations of O_3 in rural/remote areas.

1. High O_3 concentrations occur as the result of transport of "fossil"* O_3 from urban plumes.

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*Fossil O_3 is defined as O_3 which is formed on the preceding day, remains aloft overnight and is fumigated downward to the earth's surface the next day.

2. High O_3 concentrations occur as the result of transport of "partially spent" precursors from urban areas, or ozone which results from subsequent reactions of these partially spent precursors.

3. High O_3 concentrations occur as the result of in-situ emissions of fresh precursors in nearby relatively rural locations.

4. High O_3 concentrations occur naturally.

Each of these will be discussed in turn. To help us draw some conclusions regarding the relative importance of each hypothesis, 1981-83 O_3 data reported to SAROAD have been examined for sites which are not located in Metropolitan Statistical Areas (MSA's). There are some 136 such sites. Of these, 58 sites are either just outside of an MSA or can be readily associated with an MSA less than 10 hours travel time away under prevailing wind conditions. Twenty-one (21) of these 58 sites have expected exceedance rates greater than 1.0. Information concerning the remaining 78 of the 139 sites is contained in Table 4. From the information in Table 4, we see that it is quite unusual for concentrations greater than 0.12 ppm to occur at sites in SAROAD which are not obviously impacted by emissions from urban plumes less than a day's travel time away. In fact, only 13 of the 78 sites have observed any O_3 concentrations greater than the level of the NAAOS during 1981-83. Only four sites have an expected exceedance rate greater than 1.0 per year. Further implications arising from the information in Table 4 will be identified in Section 3.5. Finally, results from an application of a preliminary version of the EPA's Regional Oxidant Model will be summarized, and possible implications from these results will be identified.

TABLE 4.

NON-MSA OZONE SITES NOT CLEARLY ASSOCIATED WITH AN MSA[A]

State	Location	Site	Years	Top 3 O_3 Conc.	Avg. Exp Exc.*
AK	+ Valdez-Cordova	020565004J02	1981	.111, .096, .094	0
AZ	o Apache Sit.	030050110A08	1981-83	.075, .075, .070	0
	Flagstaff	030280004F01	1981-83	.095, .092, .092	0
	Prescott	030660002F01	1981-83	.099, .080, .077	0
	Yuma	030960003F01	1981-83	.112, .101, .100	0
CA	+ Bishop	050780001I01	1981	.080, .080, .080	0
	+ Clearlake	051390001F05	1981	.070, .050, .050	0
	+ Colusa	051520001F01	1981-83	.110, .100, .100	0
	El Centro	052240002I01	1981-83	.180, .120, .120	0.4
	Grover City	053040001I01	1982-83	.110, .100, .100	0
	+ Lakeport	053665001I01	1981-83	.080, .080, .080	0
	+ Mono Co.	054760001I01	1982-83	.090, .090, .090	0
	Morro Bay	054940001I01	1981-83	.090, .090, .080	0
	Nipomo	055150001I01	1981-83	.110, .100, .100	0
	San Luis Obispo	057040002F01	1981-83	.090, .090, .090	0
	San Luis Ob. Co.	057060001F01	1981-83	.110, .100, .100	0
	S. Lake Tahoe	057830006F01	1981-83	.100, .100, .090	0
	Ukiah	058400005I01	1981-83	.080, .080, .080	0
	+ Willows	058760001F01	1981-83	.110, .110, .110	0
	+ Yreka	058860001I01	1981-83	.070, .070, .070	0
IL	Effingham Co.	142220001F01	1981-83	.109, .102, .100	0
	La Salle	140800001F01	1981-83	.128, .127, .118	0.7
	Marion	144720001F01	1981-83	.114, .111, .106	0
	Quincy	146440005F01	1981-83	.098, .093, .091	0
IN	Kasciusko Co.	152300001F01	1981	.113, .100, .097	0
IA	Madison Co.	162360003G01	1981-83	.095, .095, .094	0
KY	Callaway Co.	180500004F05	1981-83	.143, .129, .116	0.8
	Carter Co.	180620500F05	1983	.114, .110, .109	0
	Clay Co.	180740005F05	1981-83	.107, .105, .094	0
	Falmouth	181140002F05	1981-83	.119, .113, .113	0
	Fulton Co.	181360001F05	1981-83	.105, .101, .100	0
	Hopkins Co.	181840001F05	1981-83	.135, .121, .114	0.5
	Livingston Co.	182320003F01	1981-83	.133, .122, .122	0.4
	Metcalfe Co.	182760001F05	1981-83	.109, .107, .104	0
	Muhlenberg Co.	182960005N02	1981-83	.129, .126, .106	0.7
	Ohio Co.	183080031F05	1981-83	.129, .122, .115	0.4
	Paducah	183180024F01	1981-83	.115, .114, .111	0

State	Location	Site	Years	Top 3 O_3 Conc.	Avg. Exp Exc.*
KY	Prestonburg	183400002F05	1981-83	.106, .106, .101	0
	Pulaski Co.	183460002F05	1981-83	.109, .107, .102	0
	Russellville	183600003F05	1981-83	.114, .110, .107	0
	Trigg Co.	183860001N03	1981-83	.129, .118, .116	0.4
LA	De Ridder	190800001F01	1983	.116, .081, .078	0
	Galliano	191025001F01	1983	.114, .114, .103	0
	Morgan City	191940002F01	1983	.101, .098, .096	0
ME	+ Acadia Natl. Park	200010003F05	1982-83	.138, .135, .128	3.2
	Caribou	200260001F05	1981	.070, .065, .057	0
	+ Hancock Co.	200495002F05	1982-83	.142, .125, .115	1.6
	+ Oxford Co.	200885006J02	1982	.113, .108, .105	0
MI	Marquette Co.	233280003F01	1981	.095, .085, .085	0
MN	Mankato	242100002F01	1981-82	.077, .072, .070	0
MS	Madison Co.	251720001F03	1981-82	.123, .118, .113	0
MO	+ Mark Twain Nat'l. For.	262950001A08	1981-83	.115, .115, .110	0
MT	o Custer Nat'l. For.	270310101A08	1981-83	.085, .085, .085	0
NH	Berlin	300040014F01	1981-83	.098, .097, .094	0
	Keene	300340006F01	1981-83	.135, .131, .107	1.7
NY	o Essex Co.	332020002F03	1981-83	.115, .114, .110	0
NC	+ Croatan Nat'l. For.	340945101A08	1981-83	.095, .090, .090	0
	Edgecombe Co.	341300099F05	1983	.123, .116, .108	0
	Farmville	341400099F05	1982-83	.108, .105, .099	0
	Lenior	342300003F03	1981-83	.118, .117, .113	0
	Martin Co.	342560099F05	1983	.102, .097, .094	0
	Robeson Co.	343380099F05	1982-83	.106, .101, .099	0
	Dunn Co.	350340003F03	1981-83	.081, .080, .079	0
OH	Conneaut	361480001F01	1981-83	.158, .154, .150	2.1
	Logan	363560002F01	1981-82	.110, .105, .105	0
OR	o Crook Co.	380420111A08	1981-83	.075, .065, .065	0
TN	Giles Co.[x]	441140001N03	1981-83	.012, .011, .011	
UT	Logan	460500001F01	1982	.075, .072, .072	0
	o Uintah Co.	461200001F01	1983	.070, .068, .065	0

State	Location	Site	Years	Top 3 O_3 Conc.	Avg. Exp Exc.*
VT	Brattleboro	470120002F01	1982-83	.121, .109, .102	0
	+ Green Mtn. Nat'l. For.	470265101A08	1981-82	.105, .100, .095	0
	+ Windsor	470600001F05	1981	.093, .091, .080	0
VA	Fauquier Co.	481120002F03	1982-83	.129, .120, .114	0.7
	Marion	481920005F01	1981-83	.110, .110, .100	0
WI	o Chequamegon Nat'l. For.	510490001A08	1981-82	.090, .080, .080	0
	Marathon Co.	511920991F01	1983	.101, .092, .092	0
	Platteville	512720007F01	1982-83	.107, .104, .102	0
	o Vilas Co.	513640002F05	1981-82	.088, .084, .079	0

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*Average expected exceedance calculations are estimated by averaging the computed expected exceedances for each year that a monitor was operating. It is recognized that the procedure of giving each year's calculated expected exceedance equal weight is not strictly correct in cases where sample sizes vary greatly from year to year. For the sites having non-zero expected exceedances, however, the variability in the sample size does not appear to be great.

x Decimal error?

o Remote Site

+ Site not near towns $\geq$ 5000 pop.

A All sites have at least one year in which the sample size was greater than 100.

3.1 Hypothesis 1: Transport of Fossil Ozone

This hypothesis is that relatively high concentrations of O_3 in rural/remote areas are caused primarily by O_3 transported aloft overnight and fumigated downward after sunrise on the second day. This hypothesis would also be appropriate for explaining relatively high O_3 levels occasionally seen during nighttime hours if, for some reason, the nocturnal inversion is temporarily disrupted. Ozone in urban plumes carried aloft overnight is chemically stable and not subject to dry deposition removal processes. However, it may be subject to dilution (and spreading) resulting from wind shear. Certain portions of an urban O_3 plume could be transported over large distances by "nocturnal jet" winds aloft. Because nighttime O_3 aloft is chemically stable, subject to some dilution and capable of being transported long distances, one would expect it to result in broader (geographical) peaks with lower concentrations than present in an urban plume during the first day. Further, one would expect to observe the maximum effect from "fossil" O_3 to occur in the morning after the breakup of the nocturnal inversion. Thereafter, dry deposition and possible chemical decay due to reaction with vegetative VOC emissions should reduce the impact of fossil O_3. Fossil O_3 would therefore not be expected to be of significance for more than about 24-36 hours. An exception to this generalization is possible when a plume is transported over water. In this case, the smooth surface of the water and the daytime stratification of the atmosphere resulting from the flow of warmer air over cooler water inhibit dry deposition. Altshuller (1986) cites European studies where transport of elevated O_3 concentrations over water is apparent for up to 48 hours. Because of O_3 stability over water, coastal sites might be subject to high levels of fossil O_3 at anytime of day.

Reduction of fossil O_3 from urban plumes should be subject to the same conclusions as those pertaining to the control of downwind O_3 in "one day" applications. Recall that for urban areas having NMOC/NO_x ratios about 10:1 or less, photochemical grid modeling applications suggest that controlling NMOC was uniformly beneficial, and controlling NO_x is less effective than controlling NMOC. Minor reductions in NO_x in concert with NMOC control could actually diminish the reduction in downwind O_3 arising from NMOC control in some cases.

However, in other cases having larger modeling domains, reduction of NO_x in addition to VOC appears to have beneficial effects in reducing O_3 far downwind. In the absence of regional scale model applications, the effect of NMOC and NO_x controls on fossil O_3 is best estimated on a case-by-case basis using urban scale models. In the case of grid model applications, the most useful indicator would usually be the effect of controls on O_3 predicted later in the afternoon near the downwind boundary of the grid. In the case of EKMA applications, the most useful indicator would be O_3 predicted downwind at the end of the simulation period (i.e., usually 5-6 pm).

As urban NMOC/NO_x ratios increase, the shape of the EKMA/CB3 O_3 isopleths suggests that less drastic reductions in NO_x would reduce O_3 levels downwind at the end of the first day. EKMA results suggest that even for high urban NMOC/NO_x ratios (e.g., >15:1), strategies emphasizing NO_x reduction would often require substantial NO_x controls (e.g., see Table 3) for an urban plume including high O_3 concentrations (i.e., $\geq$ 0.16 ppm) to be reduced below the level of the NAAQS. However, somewhat less reduction in NO_x might be necessary to prevent an exceedance of the NAAQS due to fossil O_3, if the fossil O_3 is subject to significant dilution overnight.

3.2 Hypothesis 2: Transport of Urban Precursors or Subsequent Products

This hypothesis is similar to the first one, except that in this case it is supposed that 2nd day elevated O_3 concentrations result not primarily from fossil O_3, but from 2nd day reactions of transported O_3 precursors. Overcast weather on the first day might result in relatively small amounts of fossil O_3 being transported. Ozone resulting from hypothesis 2 most likely would not be high in the mid-morning, as would be the case with fossil O_3. Instead, one would expect high O_3 to occur later in the day to allow transported NO_x and/or NMOC to react with each other or with locally generated precursors.

To evaluate the viability of this hypothesis, it is useful to review information regarding the chemical lifetimes of NMOC and NO_x. A review by Altshuller (1986) indicates that the chemical lifetime* of NO_x within an urban plume varies inversely with sunlight intensity as well as with the degree to which the urban plume is polluted. NO_x reacts with hydroxyl (OH) radicals or (in the absence of SO_2) with NH_3 to form nitric acid (HNO_3) or ammonium (NH_4+) salts. These products are then subject to dry deposition or absorption by water droplets so that the NO_x from which they have formed is no longer available to generate additional O_3. NO_2 is also subject to reactions with the intermediate products of reactions between aldehydes and OH radicals. The result of this latter set of reactions is peroxyacetyl nitrate (PAN). An equilibrium is established between PAN and NO_2. During the nighttime, this equilibrium favors PAN whereas during the subsequent day, conditions more favorable to the regeneration of NO_x occur. Altshuller (1986) indicates an upper limit for NO_x lifetime within an urban plume to be about 8 hours.

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*In this discussion, "lifetime" refers to the period of time required for a pollutant to decay to 37% of its original concentration, discounting the effects of dilution.

It is actually likely to be considerably less in downwind areas. Spicer (1983) has shown that lifetime of NO_x decreases rapidly at high $NMOC/NO_x$ ratios such as those in rural areas. However, it is possible for some NO_x, particularly that emitted in the late afternoon before a nocturnal inversion forms but after the period of maximum solar intensity (and OH radical concentrations), to be carried aloft overnight in the form of PAN. Nevertheless, the NO_x available in the urban plume at the end of the first day is expected to be limited (Altshuller, 1984b). Any available NO_x would be expected to rapidly decay subsequently on the second day.

Lifetimes of different NMOC species vary considerably. For example, most olefins have lifetimes shorter than NO_x, whereas the estimated lifetimes of alkanes range from 2-3 times that of NO_x to several days and longer (Altshuller, 1984b). Since the most reactive organic species do not constitute a major fraction of NMOC, we would expect to find decreasingly reactive mixes of NMOC and higher $NMOC/NO_x$ ratios as we move into more and more remote areas. Indeed, reviews of available collocated NMOC and NO_x data indicate a tendency for $NMOC/NO_x$ ratios to increase as one moves into more rural locations (OAQPS (1977)). Urban applications of EKMA/CB3 suggest that, under some circumstances, low upwind residual NMOC levels transported into cities can significantly affect VOC controls estimated as necessary to attain the O_3 NAAQS.

The foregoing information suggests that, in the absence of fresh precursor emissions, the ability of an urban plume to generate additional O_3 will eventually be limited by a lack of NO_x. Further, strategies which reduce NMOC (and as a result reduce concentrations of OH radicals) could have the potential for prolonging the chemical lifetime of NO_x. However, presence of residual NMOC in an aged urban plume could cause difficulty in meeting NAAQS for O_3 downwind of cities (Braverman, et al. 1985), (Gipson, 1984e). The preceding observations would support control of urban NO_x as a means for reducing O_3 in rural areas if it could be concluded that (a) high rural concentrations of O_3 exist independently of "first-day" plumes and (b) high rural levels of O_3 result primarily from reactions of transported precursors. We believe short lifetime of NO_x with high NMOC/NO_x ratios makes substantial production of O_3 to levels above the NAAQS unlikely. However the possibility that low O_3 levels in rural areas could be exacerbated by transported NO_x cannot be ruled out. This is because arguments for the hypothesis include the possibility that VOC-only strategies may increase NO_x lifetime and that very low NO_x concentrations are all that is believed necessary to enable measureable increases in O_3 to occur. Arguments against the hypothesis are the relatively short lifetime for NO_x and the effects of dilution introduced by overnight windshear. Better resolution of the controversy may be possible when reliable regional scale models become available. Control of NMOC to reduce residual organics in urban plumes would appear to have support from recent urban EKMA/CB3 modeling studies (Gipson, 1984e) and from recent grid model applications in Philadelphia (Braverman, et al. (1985)).

3.3 Hypothesis 3: In-situ Emissions

This hypothesis is that high concentrations of O_3 in rural/remote areas occur chiefly as the result of emissions of VOC and/or NO_x which occur in rural areas. Such emissions might include those from one or several relatively small cities/towns as well as those from large, isolated point sources of NO_x or VOC. If the cumulative effect of emissions from small towns provides the explanation for high rural O_3, one would expect to see gradual changes in O_3

throughout the day. Observed peaks would most likely occur in the afternoon. Observed high O_3 concentrations resulting from the plumes of individual point sources would most likely be characterized by sudden increases in observed O_3 levels. Impacts from such sources are likely to be highly transitory at any fixed monitor location.

Observations as well as some modeling studies suggest that buildup of O_3 within NO_x plumes from large point sources is possible. Both types of studies, however, indicate that composition of the air with which such a plume is diluted is of critical importance. For example, Altshuller (1986) cites a number of field studies in the eastern U.S. where net increases in O_3 of 20-50 ppb above background levels occur several hours downwind from the point source. Such a buildup has not been observed in rural western areas. These findings are consistent with modeling studies which predict O_3 buildups within eastern NO_x plumes which are qualitatively similar to those observed, and which predict no buildup in western areas characterized by very low background NMOC levels.

The potential for some O_3 formation by emissions from small cities/towns can be discerned from Table 4. For example, consider the rural sites reporting within the State of Arizona. With the possible exception of Yuma, these sites should be subject to similar meteorology. We note that the Flagstaff, Prescott and Yuma sites are all subject to impacts from nearby small cities/towns, whereas the Apache Sitegreaves site (Greenlee County) is more remote. We see that the O_3 levels at the remote site are lower than at the other sites.

Kelly et al. (1984) have also recently tried to assess how much O_3 observed in rural areas is potentially attributable to local emissions, as opposed to transport. These investigators conclude that most of the diurnal increases in rural O_3 which they observed were attributable to transport of O_3, but that in-situ formation from locally generated precursors is responsible for part of the increase. Interestingly, Kelly et al. (1984) conclude that in-situ formation of O_3 in rural areas can be decreased by reducing rural VOC emissions as well as NO_x emissions. This result is surprising, because one would expect NO_x control to be more effective than VOC controls in reducing O_3 generated in rural areas (where NMOC/NO_x ratios are high). If this conclusion is correct, one possible explanation may lie in the reactivity of rural mixes of NMOC. Recall from Table 3 that the "equal control" NMOC/NO_x ratio increases with decreasing reactivity of the NMOC mix. The range of reactivities considered in Section 2.0 is appropriate for urban areas. The developers of the CB-3 mechanism caution against considering reactivities outside this range with the mechanism as written (Killus et al. 1984). In order to be able to more precisely assess the relative effects of NO_x vs. VOC controls on rural sources, a more versatile mechanism is needed, and local estimates of prevailing NMOC/NO_x ratios are desirable. It may be possible to better resolve this question when more advanced mechanisms become available. In our judgment, presently available information suggests that reducing rural NO_x emissions should reduce O_3 resulting from in-situ rural reactions of NO_x and NMOC. In our opinion, the Kelly (1984) study does not represent a sufficient basis for presuming reduction in rural VOC will be beneficial in reducing O_3.

3.4 Hypothesis 4: Natural Sources

This hypothesis is that high concentrations of O_3 in rural/remote areas are attributable to natural sources. Two principal natural sources have been discussed at length in the literature: stratospheric O_3 and O_3 formed from biogenic or geogenic precursors. In a recent review, Altshuller (1983) has concluded that natural hydrocarbons do not contribute substantially to the formation of O_3 in the ambient air. Typical surface background concentrations of O_3 observed in rural areas within the U.S. during the late 1970's are in the order of 0.02-.05 ppm (Altshuller 1984a). These concentrations would constitute an upper limit for long-term surface concentrations due to stratospheric sources. However, surface concentrations substantially greater than these levels are possible for short periods. These short term excursions are not necessarily associated with meteorological conditions which ordinarily correspond with high O_3. Instead stratospheric intrusion is likely to be accompanied by strong frontal passages and "tropopause folding" events. Although these events are most likely in the spring in most parts of the continental U.S., they can occur at other times. Such episodes would be characterized by a high hourly concentration of O_3 with relatively low concentrations before and after, and would be accompanied by the aforementioned meteorological conditions.

Controlling NO_x or VOC emissions would have little effect on high surface O_3 concentrations attributable to stratospheric sources. The most appropriate strategy would be to regard stratospheric intrusions as exceptional events, and address the remaining incidences of high O_3 with one's control strategy (U.S. EPA 1986b).

3.5 Use of Ambient Data to Evaluate Hypotheses

As described earlier, O_3 data reported to SAROAD for non-MSA sites during 1981-83 have been reviewed for the purpose of evaluating each of the four hypotheses described in the preceding sections. This review can only be regarded as superficial, because meteorological data on the individual occasions have not been reviewed. However, the air quality data themselves are useful indicators of which hypotheses are most likely. In addition, Altshuller (1984a) and Martinez et al. (1979) have reviewed earlier data from special study sites. Martinez et al. (1979) conclude that all occurrences of $O_3 \geq$ 0.10 ppm observed during 1977 at 9 rural sites in the Sulfate Regional Experiment (SURE) network are attributable to "long range transport" of O_3 from urban areas. Altshuller (1986) observes that fumigation by an urban plume is the most likely and frequent explanation for high O_3 observed in rural areas. The results of the recent review are consistent with these earlier conclusions. That is, based on observed diurnal O_3 patterns and the location of rural O_3 monitors with respect to major urban centers, we believe that one day transport of O_3 from urban areas is the most common explanation for O_3 in excess of 0.12 ppm observed at rural sites. Therefore, the four hypotheses described above are useful only as possible explanations for infrequent, marginal excursions above the level of the primary NAAQS.

Table 5 identifies sites at which it is not obvious which, if any, large urban areas may cause an impact. As already noted, problems complying with the primary NAAQS are rare at such sites. Thus, it is possible to focus on the few occasions and locations for which daily maxima greater than 0.12 ppm were observed. Table 5 summarizes available information concerning instances in Table 4 where daily maximum O_3 exceeds 0.12 ppm. Each site will be briefly discussed.

The Conneaut, Ohio site's proximity to Cleveland makes it a good candidate for single day impact from a large urban area. The site's proximity to Lake Erie suggests the possibility of a lake effect, similar to that documented

TABLE 5.

RURAL SITES/OCCASIONS WITH $O_3 \geq .12$ ppm

Location	Description	Dates	Hours ≥ .12 ppm	Peak Hour	Peak Value,ppm	Most Likely Explanation*
Conneaut, OH	NE corner of Ohio, near Lake Erie, about 60 mi. NE of Cleveland Pop. ~15,000	5/22/81	1500-1900	1800	.139	u, 3
		5/23/81	1200-1800	1600	.150	u, 1
		7/16/82	1500-1600	1600	.131	u, 3
		6/11/83	1300-1700	1600	.154	u, 3
		8/19/83	1600-1700	1600	.158	u
Calloway County, KY	Small County SW corner of KY. Located in Murray (pop. ~15,000. County pop. ~28,000 Located ~35 mi. SE of Paducah (30,000); 40 mi. W. of Clarksville, TN (45,000)	7/11/81	1300 (>.100ppm, 1300-1600)	1300	.129	3
		6/8/83	1500-2000	1500	.143	3,1,2
Keene, NH	S.Central NH ~15 mi. N. of MA line. Pop. ~21,000. 40 mi. N. of Springfield, MA, 50 mi. NW of Boston	8/11/81	1600-1700	1700	.131	u, 3
		7/7/82	2000-2100	2000	.135	u, 1
Hopkins, Co. KY	Small County ~40,000 in NW KY ~30 mi. S. of Evansville, IN, (133,000) and 25 mi. SE of Owensboro (56,000) 80 mi. NW of Nashville (469,000)	9/9/81	1500 (>.100, 1400-1500)	1500	.135	u, 3, 4

Rural Sites/Occasions with $O_3 \geq .12$ ppm

Location	Description	Dates	Hours ≥ .12 ppm	Peak Hour	Peak Value,ppm	Most Likely Explanation*
El Centro, CA	Town of 21,000 in SE CA. 15 mi. N of Mexicali, MEX (264,000); ~80 mi. E of San Diego W. intervening Mtn. range.	12/20/81	1100-1300	1100, 1200	.180	u, 1, 4
Hancock County, ME	Large, rural county (~35,000) on coast in eastern Maine. Surrounds Acadia National Park	7/8/82	1800 >.100 ppm 1600-1900	1800	.125	u, 1
		8/17/83	1700-1900	1800	.142	u, 1
Fauquier County, VA	Rural (~26,000) county in N. Virginia about 30 mi. SW of DC, 30 mi. NW of Fredericksburg and 60 mi. N. of Richmond. Largest town: Warrenton (~4000).	6/23/83	1100-1700	1100	.129	u, 1, 3
Acadia National Park, ME	Coastal National Park in eastern Maine	7/4/83	1600-1700	1700	.135	3, u, 1
		7/28/83	1500 (>.100 1400-1600)	1500	.128	3, u, 1
Muhlenberg County, KY	County in W. KY. Largest towns Greenville (4000), Central City (3500). County Pop. ~27,000. Site 4.3 mi. SSE from Paradise Steam Gen. Plant. 60 mi. NNW of Nashville	7/10/83	1600-1700 (>.100 1500-1800)	1600	.129	u, 3

Rural Sites/Occasions with $O_3 \geq .12$ ppm

Location	Description	Dates	Hours ≥ .12 ppm	Peak Hour	Peak Value,ppm	Most Likely Explanation*
Ohio County, KY	County in W.KY (~19,000) Site in Dundee, about 20 mi. SE of Owensboro and 40 mi. NW of Bowling Green (40,000). 75 mi. N of Nashville.	7/11/83	1400-1700	1600	.129	3, u
Livingston County, KY	Rural County ~5000) in NW KY. Approx. 20 mi. NE of Paducah (30,000).	7/20/83	1600-1700	1600	.133	3
Trigg County KY	Rural county (~4000) at land between the Lakes Park in SW KY. 20 mi. NW of Clarksville, TN (45,000)	8/6/83	1600	1600	.129	3

*1--Transported "fossil" O_3
2--Transported, partially reacted precursors
3--In-situ formation involving local emissions
4--Natural sources
u--Impact from urban source area less than one day's travel time away

for SE Wisconsin transporting an urban plume over the lake and then onshore (Cole, et al. 1977). Secondary explanations are buildups in the late afternoon due to reactions of precursors emitted by small cities/towns. In one case (5/23/81, the 2nd day of a 2 day "episode") transport of fossil O_3 may be a viable explanation. The most likely explanation for the Callaway, Ohio, Livingston and Trigg County sites (all in Kentucky) is that generation of O_3 occurs from precursors emitted in small cities/towns. In most cases, the O_3 is relatively high for prolonged periods in the late afternoon, and there is no nearby major city. Local generation is also possible for the Muhlenberg County (KY) incident, although the relatively short distance to Nashville (~60 mi) makes a brush with that city's plume a possibility. The geographical location, as well as the timing of the Keene, NH incidents, make single day impacts from one or more large urban areas the most likely explanation for high O_3 there. The timing and short duration, as well as the location of Hopkins County, KY, suggest several possible explanations for high O_3 there, including a single day urban plume impact, stratospheric intrusion accompanying a weather front or impact from an isolated point source plume. The most likely explanation for high O_3 at El Centro, California is the site's proximity to a large city. However, the infrequency with which high O_3 is seen at El Centro as well as the timing and time of year of the incident suggest stratospheric intrusion, transport of fossil O_3 or spurious data as possible alternative explanations. The timing and duration of the incidents of Hancock County, Maine suggest single or multiday transport of O_3 from urban areas as likely causes. These explanations are possible at Acadia as well. However, the facts that high concentrations occur somewhat earlier at Acadia and happen exclusively on holidays or weekends suggest that we cannot rule out local generation at Acadia. The location of Fauquier County, Virginia as well as the length and timing of the incident there suggest the indicated three explanations as most likely.

3.6 Implications from Preliminary Applications of a Regional Scale Model

Application of the first generation of the EPA's Regional Oxidant Model (ROM 1) assessing the effect of VOC and NO_x controls over a large region has been described in a recent report by Lamb (1986). The ROM 1 application simulates emissions and meteorological conditions occurring over a 9-day period in July 1980. The modeling domain encompasses roughly a 1080 KM (E-W) X 774 KM (N-S) area in the northeastern US, centered just to the NW of Scranton (PA) and encompassing the entire northeast corridor from northern Virginia to Maine. In this study, VOC and NO_x projections between 1980-87, were made utilizing 1982 O_3 State Implementation Plans (SIP's). Although there is spatial variability in the 1980-87 projections, over the entire grid VOC emissions were reduced by 32% and NO_x emissions were diminished by 8%. Thus, the strategy could be characterized as one emphasizing VOC reductions with some supplementary reductions in NO_x. Both initial and boundary concentrations of O_3, NMOC and NO_x were assumed to be irreducible and at concentrations characteristic of natural background.

Because of uncertainty in many of the meteorological inputs (e.g., windfields) to such a model, Lamb (1986) aggregates receptor locations according to four groupings: urban, suburban, rural (agricultural) and wilderness (natural). Generally, "rural" locations are defined as being 50-100 km from an urban location and characterized by non-urban (e.g., agricultural) land use. A wilderness (natural) location is greater than 100 km from urban areas. Predicted changes in ozone characteristic of each receptor category are reported. These include changes in peak and median hourly O_3 concentrations, as well as changes in peak and median daily daylight (i.e., 7 hours: 0900-1600 Local Standard Time) average O_3 concentations*. The latter averaging time may be of interest in assessing potential effects of ozone and control programs on vegetation.

For purposes of this review, the following results of the ROM 1 application are the most pertinent:

(1) The bulk of ozone generated by VOC and NO_x emissions is produced within about 100 km of major urban areas in the northeast;

(2) In general, at any given location and hour the O_3 concentration in the control case is less than or equal to that in the base case;

(3) Within each receptor group, peak concentrations are reduced by larger percentages than the median values are reduced;

(4) Ozone is reduced more at sites near major VOC and NO_x sources than at locations far away.

(5) Similar patterns were observed for both 1- and 7-hour averaging times;

(6) Overall, the simulated strategy appears to have two effects: (a) it causes a delay in O_3 formation, and (b) it reduces the total quantity of O_3 produced;

(7) In rural and wilderness areas, maximum ozone occurred later in the simulation as a result of the strategy. Conversely, in urban and suburban areas, the strategy seemed somewhat more effective midway through the simulation.

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*As a point of clarification, in the discussion the terms "peak" and "median" refer to spatial rather than temporal peaks and medians. Thus the change in a "peak hourly O_3 concentration for wilderness areas" refers to the change in the highest hourly O_3 level observed anywhere in wilderness areas during the 9-day simulation.

As Lamb (1986) points out, results from the first generation ROM runs should be regarded as preliminary and interpreted with care. For example, ROM 1 uses an early chemical mechanism (Demerjian, et al., 1979), which may or may not be suited for rural applications. Second, several simplifications are made regarding windfields and vertical mixing. Further, biogenic emissions were not considered. In locations where NO_x is increased, this could have an effect on estimated changes in O_3 concentration. Many of these shortcomings are expected to be reduced or eliminated when the second generation ROM becomes available.

Keeping the preceding caveats in mind, the preliminary results from ROM appear consistent with many of the conclusions drawn earlier from our review of air quality data and results of urban scale model applications. For example, conclusions concerning preeminence of urban emissions in causing high rural/remote O_3 levels and the tendency of VOC reduction strategies to delay O_3 formation and shift (reduced) peaks further downwind, as well as the assertion that strategies which reduce peak O_3 downwind from cities should also have some (reduced) beneficial effect in more remote areas, are all reinforced by these preliminary findings.

3.7 Summary

It is concluded that single day transport from urban areas is frequently the most likely explanation for O_3 levels above 0.12 ppm observed at rural sites. As such, the same conclusions regarding NO_x and VOC control which were drawn in Section 2.0 for downwind areas subject to single day impacts can be drawn here. Four hypotheses have been suggested as explanations for the relatively infrequent occasions when O_3 greater than 0.12 ppm occurs at sites where single day transport from urban areas is not the obvious cause.

Even for these latter incidences, single day transport is often the most likely explanation. Of the remaining explanations, generation of O_3 from locally emitted precursors and overnight transport of fossil O_3 appear the next most likely. Presence of high $NMOC/NO_x$ ratios in rural areas suggests NO_x control has potential for reducing O_3 generated by emissions in rural areas. A more quantitative assessment awaits characterization of reactivity of rural mixes of organics, better documentation of rural $NMOC/NO_x$ ratios and applications of a chemical mechanism more suited for simulating rural O_3 formation. In cases where overnight transport of urban fossil O_3 is the most likely source of high O_3, strategies to reduce single day downwind O_3 should be effective in reducing O_3 in a rural area as well. It is not possible to make a definitive judgment regarding whether reliance on urban strategies emphasizing VOC control may exacerbate rural O_3 in areas not presently observing high O_3. However, preliminary applications of the EPA Regional Oxidant Model suggest that strategies proposed in 1982 SIP's (i.e., emphasizing VOC reduction in urban areas) may, on average, result in percent reductions in peak and typical hourly and 7-hour average O_3 concentrations in rural and remote locations which are directionally similar, but diminished from those occurring at urban/surburban sites.

4.0 Other Environmental Issues

Thus far, we have discussed relationships between control strategies and O_3 concentrations in urban, suburban and rural/remote areas. The effect of NO_x and NMOC on O_3 is the major focus of this paper. However, decisions regarding whether or not to control NO_x or VOC emissions to reduce O_3 are not made in a vacuum. Hence, it is appropriate to discuss briefly other environmental issues relating to the control of these O_3 precursors. In this section, we identify three such issues: exposure to NO_2, acid deposition, and visibility impairment.

4.1 Nitrogen Dioxide

As discussed in Section 2.0, NO_2 is formed from the oxidation of NO. There are two major pathways for this oxidation to occur: oxidation by free radicals formed from organic pollutants (i.e., photochemical synthesis) and oxidation by O_3 (i.e., O_3 titration). We have also seen that, during periods or locations where free radicals are plentiful, photochemical synthesis is the predominant pathway. Implications regarding reduction of NO_2 associated with each of these pathways were reviewed several years ago (Meyer et al. 1980). That review reached the following conclusions.

(a) Smog chamber data, empirical and chemical kinetics models all suggest that reductions in NO_x levels will lead to approximately proportional reductions in both peak and mean concentrations of NO_2. An exception to this may be the case in which peak NO_2 occurs solely as the result of titration reactions with O_3 that are limited by the amount of O_3 available.

(b) The proportionality constant between peak (and mean) NO_2 and NO_x appears to remain approximately the same for a wide variety of NMOC/NO_x ratios, emission patterns and dilution conditions. This implies that the linear rollback model has the potential to serve as a useful means for approximating the impact of NO_x controls on ambient NO_2.

(c) The information presented suggests that programs to reduce NMOC levels will not have an appreciable impact on mean NO_2. There may, however, be a small reduction in peak NO_2 accompanying reduction in NMOC for NMOC/NO_x ratios in the order of 10:1. Smog chamber data and modeling results examined imply a reduction in peak NO_2 from 0-20 percent accompanying a 50 percent reduction in NMOC.

(d) Because the proportionality constant between peak NO_2 and NMOC reduction appears to be sensitive to a number of factors, the relationship is probably not a linear one.

(e) The preceding conclusions appear valid under $NMOC/NO_x$ ratios in the order of 10:1. However, chemical kinetics model simulations (i.e., using the EKMA/DODGE model) suggest that, if the prevailing $NMOC/NO_x$ ratio is reduced to very low values (as a result of O_3 SIPs), the relative effectiveness of NO_x and VOC controls in reducing NO_2 is different. For example, for ratios of less than about 2-3:1, reduction in peak NO_2 would be more sensitive to further VOC controls than to further NO_x controls.

More recent modeling exercises conducted by SCAQMD (1982b) with the Urban Airshed model (Carbon Bond 2 mechanism) in Los Angeles also indicate that reducing NO_x emissions will reduce short-term NO_2 concentrations by varying amounts throughout the Los Angeles Basin. These results are complicated by consideration of simultaneous VOC control strategies, non-uniform spatial application of the VOC and NO_x strategies, and the impact of the NO_x and VOC strategies on the geographical location of the NO_2 peak. Given the preceding complications, the analysis suggests that reductions in NO_x may result in reductions in peak NO_2, which are less than proportional. Similar results have been obtained in preliminary analyses available for Philadelphia (Burton 1985).

Presently, the NAAQS for NO_2 is one which requires the annual arithmetic mean concentration to be no greater than 0.053 ppm. OAQPS (1986) has compiled a list of locations with observed, annual average NO_2 values greater than

0.035 ppm. This is shown in Table 6. As Table 6 indicates, there are relatively few locations with annual NO_2 levels approaching the NAAQS, and only one (Los Angeles) where the NAAQS was exceeded. Meyer et al. (1980), have reviewed high hourly NO_2 data reported to SAROAD in the late 1970's. This review implies that, unless a short term NAAQS less than about 0.30 ppm is promulgated, the need to meet NO_2 NAAQS is not going to provide a strong rationale for additional national emission control programs to reduce NO_x unless or until long-term growth threatens to result in increased emissions.

4.2 Acid Deposition/Visibility Impairment

Acid deposition and visibility impairment have been lumped together in this discussion for several reasons. First, with the exception of some regulations to protect visibility in Class I (primarily rural) areas, there are no major Federal regulatory programs currently in effect which specifically deal with these issues. Nevertheless, both issues are currently being studied by the Agency, with a view towards the need for possible future regulatory programs. Thus, strategies for dealing with NO_x and NMOC to reduce O_3 should try to avoid exacerbating these other problems. Second, many of the same processes thought to result in acid deposition are also thought to be important contributors to visibility impairment. Third, the ability to quantify the effects of VOC and/or NO_x controls on visibility and acid deposition is more uncertain then is the case for O_3 or NO_2. As a result, conclusions in this section should be viewed as more qualitative and preliminary than others presented in this report.

4.2.1 Acid Deposition

The two major acidic species contributing to acid deposition are sulfuric acid (H_2SO_4) and nitric acid (HNO_3) (NRC, 1983, NCAR, 1983). Acidic species

TABLE 6

ANNUAL ARITHMETIC MEAN NO_2 CONCENTRATIONS*

MSA	Site	Concentration, ppm	Year
Boston, MA	220240002F01	.044	1984
Nassau-Suffolk, NY	332900005F01	.035	1984
New York, NY-NJ	334680010F01	.041	1984
Baltimore, MD	210120040F01	.036?	1984
Philadelphia, PA-NJ	397140047H01	.040	1984
Chicago, IL	141340001G01	.052	1982
Nashville-Davidson, TN	442540011G01	.053?	1982
St. Louis, MO-IL	264280072H01	.035?	1984
Denver-Boulder, CO	060580002F01	.052	1983
Salt Lake City-Ogden, UT	460920001F01	.037	1984
Anaheim-Santa Anita-Garden Grove, CA	053620001I01	.048	1982
Los Angeles-Long Beach, CA	050900002I01	.062	1982
Riverside-San Bernardino, CA	056680003I01	.043	1982

*Values shown are the maximum annual mean observed between 1982-84.

? = Mean calculated from 50-75% of maximum potential number of observations.

may be formed by one of two methods: (1) through gas phase oxidation, or (2) through absorption of precursor(s) by liquids and subsequent liquid phase oxidation.

Gas phase reactions of importance include the following:

$$SO_2 + OH \xrightarrow{H_2O} H_2SO_4 + HO_2 \text{ (hydroperoxy radical)} \qquad (1)$$

$$NO_2 + OH \longrightarrow HNO_3 \qquad (2)$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \text{ and } N_2O_5 \xrightarrow{H_2O} {}^2HNO_3 \qquad (3)$$

Liquid phase reactions thought to be significant are:

$$SO_2 + H_2O_2 \text{ (hydrogen peroxide) } \xrightarrow{H_2O} H_2SO_4 + O_2 \qquad (4)$$

$$SO_2 + O_3 + H_2O \longrightarrow H_2SO_4 + O_2 \qquad (5)$$

and, under some circumstances

$$SO_2 + 1/2\ O_2 \xrightarrow{Fe^{+3},\ Mn^{+2},\ H_2O} H_2SO_4 \qquad (6)$$

Nitric acid formation occurs about 10 times faster than sulfuric acid formation, and results almost exclusively from gas phase oxidation. Reaction (2) is thought to be the principal pathway for HNO_3 formation. Sulfuric acid results both from gas and liquid phase oxidation, with reactions (1), (4) and (5) thought to be the most significant. Above pH of about 5.5, reaction (5) is probably of greatest importance among the liquid phase reactions (Scire, et al. 1985b). However, reactions (5) and (6) are self-limiting. For example, for pH less than 4.0, the H_2SO_4 production rate from reaction (5) is only about 1 percent that of reaction (4). Thus, the reaction of SO_2 with hydrogen peroxide (H_2O_2) (reaction 4) may be of particular importance. In glancing at reactions (1), (2), (4) and (5), we see that they involve a number of species which are formed in the sequence of photolysis/oxidation reactions involving NMOC/NO_x/O_3. For example, formation of H_2O_2 results from hydroperoxy (HO_2) radicals, which themselves result from photolysis of aldehydes. Hydrogen peroxide is also limited by competing reactions involving formation of NO_2 from NO. Hydroxyl (OH) radicals are formed in the oxidation of NO to NO_2 by HO_2, among other species. Presence of NO, NO_2 and O_3 is also noted. Thus, strategies involving changes in NO_x and/or NMOC levels could have a potentially significant impact on formation of acidic species. In the following paragraphs, pertinent results of recent experimental and modeling studies are identified.

Spicer (1983) has studied formation of NO_x oxidation products (i.e., HNO_3 and PAN) in smog chamber experiments. In these experiments, a 17 component synthetic urban mix was irradiated in an indoor chamber under low humidity and little or no SO_2. NMOC/NO_x ratios in the 18 experiments varied from about 4-63:1. As the initial NMOC/NO_x ratio was increased, the rate at which NO_x formed oxidation products increased. Thus, the lifetime of NO_2 at an NMOC/NO_x ratio of 20:1 was only about one hour. In addition, HNO_3 formation was found to be directly proportional to the initial concentration of NO_x in the experiments, regardless of the NMOC/NO_x ratio. Thus, the ratio of PAN/HNO_3 also increased with increasing NMOC/NO_x ratios.

Kleinman (1984) has examined liquid-phase oxidation of SO_2 more closely using a simple storm model. Based on an analysis of precipitation data obtained in the Northeast, Kleinman concluded that in-cloud oxidation of SO_2 accounts for 46-66% of summertime $SO_4^=$ (sulfate) formation. When this range of values was used in his simulation model, Kleinman concluded that an amount of H_2O_2 greater than that predicted by many photochemical models is required to account for sulfate formation (i.e., H_2O_2 concentrations of roughly 4 ppb would be necessary to account for $SO_4^=$ observed in rainwater, whereas only about 1 ppb H_2O_2 is believed available). If it is true that SO_2 to sulfate conversion at low pH's (i.e., pH < 4-5) is limited by processes in the $NMOC/NO_x/O_3$ photolysis oxidation cycle which affect the production and accumulation of H_2O_2, control of NO_x may have an effect on liquid phase formation of H_2SO_4. As we have previously noted, H_2O_2 is formed by combination of two hydroperoxy (HO_2) radicals. However, HO_2 also oxidizes NO to NO_2. Thus, reducing NO_x could increase the availability of HO_2 to form H_2O_2. Increased production of H_2O_2 could increase liquid phase formation of H_2SO_4 (reaction (4)).

The issue of liquid phase conversion of SO_2 to $SO_4^=$ has also been investigated by Scire et al. (1985b). These authors use a chemical model to hypothesize that, except at very low SO_2 concentrations, liquid phase SO_2 to $SO_4^=$ conversion is first importantly influenced by availability of oxidant (i.e., H_2O_2) but is ultimately limited by pH. That is, after the small amount of available H_2O_2 (e.g., 1 ppb) is exhausted, conversion takes place largely as the result of reaction with O_3 via reaction (5). Since background levels of O_3 would be more than enough to convert all available SO_2, conversion is ultimately limited by pH. Availability of NH_3 can increase SO_2 to $SO_4^=$ conversion by raising pH. However, the acidity of the liquid droplet is limited by the fact that reaction (5) is pH limited. A key insight offered by Scire et al. (1985b) is the timing or sequence with which various liquid phase reactions converting SO_2 to $SO_4^=$ come into play. If available H_2O_2 is eliminated before pH becomes a limiting factor in reaction (5), then the role of NO_x control on liquid phase formation of H_2SO_4 may be less important than would otherwise be the case.

Seigneur et al. (1984a,b) have also developed and described applications of a model for acidic species formation. The model is a box model which starts with the CB-3 mechanism and adds several reactions to take more detailed account of $SO_4^=$, NO_3^- and H_2O_2 chemistry (Seigneur et al. (1984a)). In the model, transfer between gas and liquid phases is limited by liquid phase reaction rates, and, like the Scire et al. model, the ultimate amount of gaseous material absorbed into the liquid is limited by Henry's Law. Model predictions are qualitatively consistent with composition of rain/cloud water at three locations (Seigneur et al. 1984a).

The Seigneur model has been used to note the impact of SO_2, NO_x and NMOC on sulfate (H_2SO_4) and nitrate (HNO_3) formation under clear skies and within stratus clouds, during both summer and winter. Table 7 has been adapted from one appearing in Seigneur et al. (1984b). We see that, under clear sky (dry) conditions, reductions in SO_2 and NO_x lead to approximately proportional reductions in $SO_4^=$ and NO_3^- respectively, according to the model. Reductions in NO_x also result in small reductions in $SO_4^=$. Reductions in NMOC result in small, counterproductive changes in summer and small reductions in $SO_4^=$ during winter. Seigneur (1983) has explained these findings in terms of counterveiling effects resulting from reductions of OH and HO_2 radical production versus longer lifetimes and reaction cycles for those OH radicals which remain.

Table 7 indicates greater non-linearities in the relationships between $SO_4^=$, NO_3^- and their precursors when cloud chemistry is introduced. We see, for example, that reduction of SO_2 and NO_x continue to be beneficial in reducing predicted levels of $SO_4^=$ and NO_3^-, respectively. However, in the presence of

TABLE 7.

CHANGES IN SULFATE AND INORGANIC NITRATE CONCENTRATIONS DUE TO REDUCTIONS IN PRECURSOR CONCENTRATIONS*

Variable	ΔSO_2 = -50%		ΔNO_x = -50%		ΔNMOC = -50%	
Conditions	June	December	June	December	June	December
Clear Sky						
Sulfate	-48%	-48%	-18%	-9%	+9%	-9%
Nitrate	+1%	0	-55%	-58%	+11%	+4%
Stratus Clouds						
Sulfate	-22%	-26%	+30%	+33%	-7%	-5%
Nitrate	0	+2%	-41%	-32%	-9%	-9%
Estimated Overall Effect						
Sulfate	-35%	-37%	+6%	+12%	+1%	-7%
Nitrate	+1%	0	-55%	-58%	+11%	+4%

*After Seigneur, et al. (1984b)

cloud water, reduction in NO_x apparently has a fairly substantial counterproductive effect on $SO_4^=$ production. Seigneur et al. (1984 a) attribute this finding to lower reactivity of the cloud system which leads to a net increase in OH radicals in the cloud environment. The "estimated overall effect" numbers in Table 7 have been derived for illustrative purposes, assuming that HNO_3 production results almost entirely from gas phase oxidation, whereas gas and liquid phase oxidation are roughly of equal significance in H_2SO_4 production. Using these assumptions, the Seigneur et al. (1984 b) modeling results imply that NO_x control will lead to approximately proportional reductions in HNO_3. However, some small increase in H_2SO_4 may result. The model predicts that reducing NMOC will have relatively little effect on HNO_3 or H_2SO_4 concentrations.

Scire, et al. (1985a) have utilized a regional scale grid model to simulate the effect of 50% reductions in VOC, NO_x and SO_2 on wet, dry and total deposition of sulfur averaged over a single 7-day period in July 1980. The model adds wet chemistry to a gas-phase chemical mechanism described by Lurmann, et al. (1984). The modeling domain in this study covers roughly the eastern one-half of the United States as well as southern Ontario and Quebec. The results are qualitatively similar to those reported by Seigneur for acidic species formation. For example, for the modeled period, Scire et al. found a 50% reduction in VOC resulted in little change in wet, dry or total sulfur deposition and only a slight increase in average $SO_4^=$ concentrations (2-4%). HNO_3 concentrations typically increased by 4% or less. A 50% reduction in NO_x emissions led to a typical net change in total sulfur deposition of ±5%, while $SO_4^=$ concentrations were reduced 12-14% over a large portion of the grid. As with the Seigneur model, a 50% reduction in NO_x emissions led to a nearly proportional reduction in HNO_3 over large areas of the grid.

Several caveats with regard to the preceding discussion are in order. First, the Seigneur and Scire (1985b) studies address formation of acidic species rather than deposition. Formation of acidic species per se may not completely describe the potential for acid deposition. For example, it is believed that the dry deposition velocity for SO_2 is relatively high. Once removed from the atmosphere, SO_2 may behave as an acid. Preliminary, limited regional scale studies by Scire et al. (1985a) suggest that neither VOC nor NO_x control are likely to have major effects on SO_2 concentrations averaged over several days and distances of 80 km or more. Further, once SO_2 remaining in the atmosphere is converted to $SO_4^=$ by gas phase reactions, little deposition is likely to occur until the $SO_4^=$ is absorbed by droplets and precipitation occurs. Second, the Seigneur model has not as yet been applied to simulate environments other than clear skies or stratus clouds. For example, results simulating acidic species formation in stratocumulous clouds or in precipitating clouds have not been reported. If these latter environments are relatively important in contributing to acid deposition (compared to clear sky or stratus cloud environments), the generality of conclusions regarding NO_x and NMOC vs. acid species formation may be questioned. Similarly, the regional scale model application described in Scire et al. (1985a) represents a single incident and this model is still evolving. Finally, in the preceding discussion we have ignored seasonal effects. It has been suggested, for example, that HNO_3 formation may be of greatest concern in the winter and spring due to the effect of "acid shock" accompanying snow melt. If this is indeed the case, mechanisms which are effective in forming HNO_3 under low temperatures or limited sunlight may be of somewhat greater importance than implied in our discussion.

4.2.2 Visibility Impairment

This discussion is confined largely to the "regional haze" phenomenon as opposed to impacts from individual plumes ("plume blight"). Secondary particulate matter, formed as the result of chemical reactions in the atmosphere, is generally believed to be an extremely important cause of regional visibility extinction. Table 8 provides estimates of the relative importance of various elements leading to visibility attenuation in the eastern U.S. (SAI, 1985). In the eastern U.S., sulfate aerosol is the single most important cause (>50%) of regional visibility extinction. Secondary organic aerosol is also believed to be of some minor significance. Remaining causes include primary fine particulate (mostly carbon particles) and NO_2. In addition to sulfates ($SO_4^{=}$) formed as the result of reactions (4), (5) and (6) and reaction (1) followed by absorption by water droplets, reaction of SO_2 or H_2SO_4 vapor with ammonia (NH_3) is an extremely important source of $SO_4^{=}$ aerosol resulting in visibility attenuation in the East.

The consensus at present is that nitrate (NO_3^-) aerosol is a relatively unimportant source of visibility impairment in the East. For example, limited measurements in the Smoky Mountains indicate particulate NO_3^- levels are about 1-2% of measured fine particulate matter whereas $SO_4^{=}$ constitutes about 50% of the mass of fine ($\leq$ 2.5 µm) particulate matter (Stevens et al. 1984). One reason for the limited influence of particulate NO_3^- on visibility in eastern rural areas is that the reaction between NH_3 and $SO_4^{=}$ is much faster than the reaction of NH_3 with NO_3^- (SAI, 1985). In the East, where there is plenty of sulfate, there is insufficient NH_3 to convert gaseous HNO_3 to NO_3^- aerosol. Recent measurements conducted in Warren, Michigan by Cadle (1985) indicate particulate NO_3^- levels ($\leq$ 1.1 µm) of about 2 $\mu g/m^3$.

TABLE 8

PERCENT CONTRIBUTIONS OF VARIOUS SPECIES TO LIGHT EXTINCTION IN "TYPICAL" URBAN AND NONURBAN ATMOSPHERES IN THE EASTERN U.S.

Species	Percent of Total Extinction		Percent of Anthropogenic Extinction	
	Urban	Nonurban	Urban	Nonurban
Blue-sky Rayleigh scatter	5.3	45.9	0	0
Fine Particles (< 2.5 μm)				
$SO_4^=$ (+H_2O)	14.8	18.3	16.0	52.6
NO_3^- (H_2O)	6.8	0	6.9	0
Elemental carbon	34.2	6.0	37.2	17.1
Primary Organic Carbon	14.2	2.8	15.4	7.9
Secondary Organic Carbon	3.2	13.8	1.7	0
Other	9.5	1.4	10.3	3.9
Subtotal	82.3	42.3	87.5	81.5
Coarse Particles (2.5 μm < d ≤ 10 μm)				
Soil dust	0.6	1.8	0	0
Anthropogenic	1.9	5.5	2.1	15.8
Subtotal	2.5	7.3	2.1	15.8
Other TSP (> 10 μm)	1.1	3.7	0.7	0
Nitrogen Dioxide Gas (NO_2)	9.0	0.9	9.7	2.6
Total	100.0	100.0	100.0	100.0

Source: SAI (1985)

This is approximately 20-50% of the $SO_4^=$ levels at the same site, depending on the season of the year. Thus, it is possible that particulate NO_3^- may be somewhat more important in reducing visibility in urban areas. In the Western U.S., where there are generally very low levels of SO_2 or sulfate, HNO_3 vapor may be neutralized by ammonia to form ammonium nitrate (NH_4NO_3) aerosol. Hence, reduction of HNO_3 in the West may improve visibility there. We might also speculate that if vigorous programs to reduce SO_2 are undertaken in the East and NO_x emissions are not reduced, visibility improvement might be less than anticipated. This would presumably follow from greater availability of NH_3 to form NO_3^- aerosol.

The Seigneur model, described previously, has been applied to estimate the effect on visibility of reducing NO_x by 9%. The results have been summarized by SAI (1985). According to the model, visibility is likely to improve due to reduction in NO_2 and (in the western U.S. only) as a result of reduced HNO_3. Increases in H_2O_2 production resulting from NO_x control should increase liquid phase $SO_4^=$ formation and thereby reduce visibility. Ambivalent impacts on OH radical concentrations will lead to ambivalent impacts on visibility. In summary, SAI (1985) estimates that a 9% reduction in NO_x will lead to a ±4% change in visibility in the East and a +8% to -4% change in the West.*

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*"+" denotes an improvement in visibility in this context.

5.0 Summary, Conclusions And Implications

In this review, we have considered potential consequences of controlling VOC and NO_x with respect to:

(1) O_3 concentrations in urban plumes within one day's travel time of the urban source of precursors;

(2) O_3 concentrations observed in rural/remote areas;

(3) peak and mean concentrations of NO_2;

(4) formation of acidic species which may ultimately lead to acid deposition, and;

(5) formation of aerosols which may lead to visibility impairment.

5.1 One-Day Ozone Phe[illegible]non

Our review suggests th[illegible]rolling VOC and controlling NO_x both have the potential to reduce peak O_3 concentrations in urban plumes. Whether or not reductions will actually occur depends on a host of factors, including prevailing NMOC/NO_x ratios, reactivity of the NMOC mix and severity of the city's O_3 problem. EKMA/CB3 analyses reported herein indicate that VOC control strategies are likely to be most effective if the prevailing morning NMOC/NO_x ratios are less than about 10:1. Preferences for a VOC strategy should increase as the reactivity of an area's NMOC mix decreases and as the severity of a city's O_3 problem and the dilution to which an urban plume is subject, increase. Thus, a city may well have an "Equal Control Ratio" (ECR) greater than 10:1 if any of the following occur: a relatively unreactive mix of NMOC, high dilution, severe O_3 problems (e.g., peak $O_3 \geq 0.18$ ppm). Further, if one assumes that control costs associated with major NO_x reductions are greater than those associated with major VOC controls, in areas with severe O_3 concentrations a VOC control strategy may be preferable to an NO_x control strategy at NMOC/NO_x ratios greater than the ECR's reported in this review. Under the most likely conditions in urbans areas with $O_3 \geq 0.14$ ppm, it is improbable that a strategy emphasizing NO_x control would be preferable to a VOC strategy unless the prevailing NMOC/NO_x ratio were greater than about 20:1.

The preceding EKMA analyses address the effects of VOC and NO_x control strategies on peak O_3. However, the change in the magnitude of the peak O_3 concentration does not tell the whole story. It is informative to compare columns (12) and (13) in Table 1. The prevailing morning NMOC/NO_x ratios in Los Angeles are thought to be about 10-11:1, and we see that 50% reductions in NMOC and NO_x result in comparable reductions in predicted Basinwide peak O_3 (-19%). However, the NO_x strategy, while reducing the peak, shifts it in, closer to the sources of NO (and the population centers). Although not apparent from Table 1 (because the base peak is predicted to occur at the furthest location downwind already), the Kumar et al. (1984) trend analysis suggests that an NMOC strategy reduces the peak and tends to shift it out, away from the population centers. This outward shift is consistent with findings reported from modeling studies in St. Louis (Gipson 1982).

Furthermore, Table 1 indicates that there is a marked adverse effect associated with the NO_x strategy which occurs in heavily populated areas closer in to the city than where the predicted peak lies (at the DOLA and Anaheim sites, for example). However, trend data from the South Coast Air Basin suggest that this adverse effect can be diminished by selectively controlling sources of NO_x and by concurrently controlling VOC emissions. In short, in a strategy emphasizing NO_x control, things could get worse in the most heavily populated areas before they get better. In contrast, improvement in O_3 levels closer in than the peak are noted with the VOC strategy. Since an NO_x strategy may likely lead to a temporary deterioration in O_3 concentrations in the most populated areas, it is, perhaps, even more important that the prescribed NO_x reductions (made with little accompanying VOC reductions) be implemented expeditiously than is the case for VOC controls under a VOC control strategy.

Trend data and modeling results suggest that strategies in which some NO_x reduction accompanies VOC reductions may be more effective than VOC-only strategies in reducing peak O_3 to the level of the NAAQS under some conditions if $NMOC/NO_x$ ratios are about 10:1 or greater. Such a strategy could also have the potential for reducing peak O_3 more rapidly than a VOC-only strategy in some cases.

Although we have used "Equal Control Ratios", which we have derived from our analyses, we have also noted that they can be sensitive to factors which may vary from location to location. Further, there are risks associated with increased population exposure to O_3 greater than 0.12 ppm associated with an NO_x strategy. Therefore, it is advisable for each individual city considering a strategy incorporating some NO_x in addition to VOC controls to generate a city-specific EKMA isopleth diagram reflecting appropriate assumptions concerning dilution, post-8AM emissions and, if possible, reactivity. A relatively simple check to insure that populated areas will be adequately protected during the period before the full effect of the NO_x strategy is realized, would be to review present NO_x and O_3 concentrations during periods of high photochemical activity (e.g.,~10AM - 4PM). If the sum of the (O_3 + NO + NO_2) concentrations for each hour at each site in the urban core (i.e., where the potential adverse effect of NO_x control may be greatest) is less than 0.12 ppm, reduction in NO_x should not lead to an excursion above the level of the NAAQS where none existed before. Alternatively, a more sophisticated analysis with an Eulerian photochemical grid model could be performed to insure the strategy is not likely to exacerbate O_3 concentrations above the level of the NAAQS in populated areas. A third alternative might be to selectively reduce NO_x only at those sources not likely to impact nearby ground level concentrations of O_3. Barring such an individual analysis, we conclude that strategies emphasizing VOC reductions (with or without small relative reductions in NO_x) remain the safest, most effective means for reducing urban O_3 levels.

5.2 Ozone in Rural/Remote Areas

From our review of O_3 observed in rural areas, we conclude that the great majority of observed concentrations $\geq$ 0.12 ppm result from urban plumes originating from large cities less than a day's travel time away. In our discussion of the "single day phenomenon" above, we note that an urban VOC control strategy, while reducing peak O_3, may shift the peak further downwind. Hence, the possibility exists that such a strategy could exacerbate O_3 levels far downwind but still within a single day's travel time. We also note that strategies to reduce urban NO_x drastically may realize their greatest potential benefits far downwind. In our opinion, the VOC strategy is not likely to lead to significant increases in O_3 levels further downwind than the site of the peak O_3. This opinion is based on two findings, both of which have to do with timing. First, it takes several hours (e.g., up to 10) for an urban plume to reach the locations we are concerned about. However, we have seen that NO_x has a relatively short lifetime, even at low NMOC/NO_x ratios. Past reviews (OAQPS, 1977) have indicated NMOC/NO_x ratios increase further downwind. This, by itself, would tend to decrease the lifetime of any remaining NO_x still further. Second, by the time a plume reaches these far downwind areas, the sun has passed its zenith by several hours. Hence, the photolysis/oxidation cycle has begun to slow down and is less likely to be able to compensate for the effects of dilution.

Our conclusions are consistent with the 1965-80 O_3 trend data from San Bernardino. We note that the O_3 trend in San Bernardino increases slightly over this period coincident with larger reductions in VOC than NO_x emissions upwind. This small upward trend could be reflective of the migration of the population and emissions further east (i.e., downwind). In contrast, the Urban Airshed Modeling analyses, in which uniform control strategies are simulated for Los Angeles, predict reductions in O_3 at the farthest reaches of the modeling domain (~75 miles) accompanying all simulated VOC reduction strategies. We therefore conclude that if a city's VOC strategy is sufficient to reduce peak downwind concentrations of O_3, O_3 concentrations even further downwind but within one day's travel time should also ordinarily be reduced, but possibly by a smaller percentage. For a given reduction in peak O_3 concentration, benefits of NO_x control may exceed those of VOC control at such downwind sites. If such an additional benefit occurs, it would do so because the peak O_3 concentration is likely to occur further upwind and sooner under an NO_x control strategy. Hence, these high concentrations will be subject to further dilution before reaching remote/rural areas.

Our review of high O_3 in rural/remote areas suggests that other potential explanations result in high O_3 much less frequently and in more moderate levels than does the single day phenomenon. We have examined four hypotheses: (1) transport of fossil O_3; (2) transport of precursors; (3) in-situ formation due to "rural" emissions; and (4) natural causes. Of these, natural causes (i.e., stratospheric O_3) should be distinctive by its accompanying meteorology, and may further be identified by a distinctive diurnal pattern and time of year in which it occurs. Hypothesis 3 appears to be the most likely of the remaining three explanations. Reduction of NO_x emissions occurring in rural areas appears to have potential for reducing rural O_3. More quantitative estimates would require one to characterize NMOC/NO_x ratios, estimate the reactivity of the rural mix of NMOC and apply a model incorporating a chemical mechanism adapted for use for a rural mix of NMOC. Reduction in fossil O_3 should accompany urban reductions of NMOC or NO_x providing these controls are successful in reducing first day peaks. We believe hypothesis 2 (with regard to NO_x) is the most difficult of the hypotheses to evaluate. Unless NO_x is replenished by fresh emissions toward the end of the first day, NO_x levels in the plume at the end of the first day are likely to be very low. Even if the fresh emissions occur and the NO_x survives as PAN overnight, the next day it is likely to decay rapidly (with the high rural NMOC/NO_x ratios). However, it may take only very small increases in NO_x to increase ozone forming capacity in rural/remote areas somewhat. Hence, some increase in rural O_3 due to increased transport of NO_x cannot be ruled out. With regard to NMOC transport, we have seen that transport of NMOC into NO_x-rich areas (i.e., cities) can be an important factor in urban attainment demonstrations under some circumstances. We expect upwind strategies to control NMOC will reduce some of this transported precursor. Preliminary results obtained in an application of a regional scale model are consistent with expectations derived from our analysis of air quality data. That is, most O_3 appears to result from urban emissions of VOC and NO_x, and strategies emphasizing VOC reduction appear to reduce O_3 in remote areas though by a smaller percentage than is true in urban/suburban areas.

5.3 NO_2

Our review indicates that reducing NO_x should also reduce peak and mean levels of NO_2, whereas reducing NMOC has a relatively small, uncertain impact on peak NO_2 only. Most recent analyses suggest that reduction in peak short-term NO_2 may be slightly less than proportional to reductions in NO_x. Our review of current data indicates that existing NAAQS for NO_2 are threatened in only a few locations. Therefore, from a national perspective, immediate concern for reducing current levels of NO_2 may deserve a lower priority than concern for reducing current levels of O_3.

5.4 Acid Deposition and Visibility

Two major acid species are of concern: HNO_3 and H_2SO_4. HNO_3 is thought to form almost entirely from gas phase reactions, and appears to be directly proportional to available NO_x. Hence, strategies to reduce NO_x should be effective in reducing HNO_3 vapor. Gas and liquid phase oxidation both are of potential importance in the formation of H_2SO_4. Reduction of NO_x appears to have a small benefit in reducing gas phase formation of H_2SO_4. However, in a stratus cloud environment, competing processes appear to cause NO_x control to lead to fairly substantial increases in H_2SO_4 production. These observations lead us to conclude that NO_x reduction in the west (or in other areas where there are low $SO_2/SO_4^=$ levels) should reduce the concentration of acid species and, most likely, the potential for acid deposition. In the east, where there is ample $SO_4^=$, the picture is less clear. To get a more quantitative assessment, it would be necessary (1) to estimate the relative importance of liquid phase vs. gas phase formation of H_2SO_4, (2) to estimate the relative abundance of H_2SO_4 vs. HNO_3, and (3) to estimate the relative importance of dry vs. wet deposition. If we assume that (1) gas and liquid phase oxidation are roughly of equal importance for H_2SO_4, (2) H_2SO_4 and HNO_3 are about equally abundant and (3) wet and dry deposition are about equally important, then reducing NO_x should reduce the presence of acid species and deposition in the eastern U.S. according to available models. The impact of reducing NMOC on concentrations of acidic species appears to be small and ambiguous, according to the same models.

Secondary aerosols are the primary cause of regional visibility attenuation. Sulfate particles are of particular importance. Sulfate aerosol consists primarily of (1) H_2SO_4 droplets, formed by liquid phase oxidation or by gas phase oxidation followed by absorption and (2) $(NH_4)_2SO_4$ particles formed from reactions between SO_2 or H_2SO_4 and NH_3. In locations where $SO_4^=$ is sparse, NO_3^- aerosol may be of some significance in reducing visibility as a result of reactions betweeen HNO_3 vapor and NH_3. In addition, NO_2 may lead to some visibility attenuation in urban areas. Hence, in the western U.S., reduction of NO_x could improve regional visibility. In the eastern U.S., the effect of NO_x control on visibility would depend on the relative importance of aerosols formed by reaction of H_2SO_4 vapor with NH_3 vs. aerosols which depend on liquid phase reactions to form $SO_4^=$. The possibility exists that major programs to reduce $SO_4^=$ (to improve visibility) may be less than successful unless NO_x emissions are also reduced.

5.5 Implications

5.5.1 Implications for Further Studies

1. Efforts should be undertaken to better define NMOC/NO_x ratios as well as ambient NMOC and NO_x concentrations prevailing in urban areas.

The effectiveness of NMOC vs. NO_x controls for a particular city depends on the relative amounts of NMOC and NO_x present. Potential detrimental impacts of NO_x control near populated areas should depend on present levels of NO_x as well. Recent development of the cryogenic preconcentration approach for measuring NMOC makes these measurements more reliable than formerly. Monitoring these ratios may lead to more enlightening O_3 trend analyses. The following might be considered as follow-up activities:

(a) Select a limited number of pilot cities to begin measurement of NMOC with collocated NO_x in at least two locations per city.

(b) Scrutinize NO_x measurements more closely than before using methods such as those proposed by Richter et al. (1979) and closer checks on equipment and procedures. Such efforts are needed to more completely ensure that high quality data underlie calculation of NMOC/NO_x ratios.

(c) Re-examine reasons for apparent discrepancies between ambient NMOC/NO_x ratios and those derived from emission inventories by reviewing appropriate files from past runs of the Urban Airshed Model and by comparing measured 6-9AM ratios with those derived using other procedures such as the one recommended by Killus et al. (1984).

(d) Continue efforts to evaluate the NMOC cryogenic preconcentration technique and to make it more useable by State/local agencies.

(e) Conduct a limited number of special studies to characterize NMOC/NO_x and reactivity in small cities/towns and surrounding rural countryside.

(f) Evaluate alternative means for estimating NMOC/NO_x ratios, such as measurement of NMOC/(NO_x + PAN + HNO_3 + NO_3^-) ratios at sites observing high O_3.

(g) Investigate potential usefulness of individual NMOC species as tracers for source categories or as indicators of reactivity. Perform species measurements periodically in conjunction with NMOC measurements.

2. Efforts should be continued to develop and evaluate chemical mechanisms which are readily adaptable for considering both urban and rural situations.

To pursue this implication, we suggest consideration of the following activities.

(a) Continued support should be given for development and sensitivity testing of the CB-X and ALW chemical mechanisms.

(b) Appropriate default assumptions (e.g., reactivity, levels and composition of transported precursors, etc.) should be developed for use with these mechanisms.

(c) Incorporation of these mechanisms (or simplified versions) into the computer model used in EKMA and into more sophisticated photochemical dispersion models should be undertaken. Further assessment of the effects of using different chemical mechanisms on the evaluation of control strategies should be made using a standardized testing protocol.

3. Additional sophisticated modeling of implications arising from VOC vs. NO_x control should be undertaken. These efforts are needed to test the generality of conclusions drawn from the Los Angeles, San Francisco and St. Louis modeling studies. They are also needed to more fully substantiate and quantify conclusions which we have drawn concerning effects of controls on high O_3 levels in rural/remote areas, as well as on O_3 levels lower than 0.12 ppm which may be of concern for a secondary NAAQS or for future primary NAAOS.

To support such modeling work, we suggest consideration of the following items.

(a) Continue development of the Regional Oxidant Model (ROM) and carefully select strategy scenarios involving VOC control, NO_x control and measures to control both precursors. These scenarios should be used to develop more quantifiable impacts on O_3 in rural/remote areas.

(b) Perform an urban scale modeling study in which the modeling domain extends further downwind than was the case in the St. Louis Urban Airshed Model Studies, and perform a more extensive set of strategy simulations to assess relative merits of VOC vs. NO_x control.

(c) Perform Urban Airshed Model strategy simulations for a smaller city, having potentially higher NMOC/NO_x ratios and an NMOC mix having some potential for differing from the default mix. Since the model has already been run and evaluated in Tulsa, Oklahoma, this might be a logical location for such work.

4. The Seigneur and Scire (1985b) models for acid species and secondary aerosol formation need to be evaluated more extensively and reconciled, as does the model described by Scire et al (1985a). In addition, efforts should be made to investigate the suitability of models to predict NO_2, O_3, acid species and aerosol formation in and on the fringes of NO_x and NMOC point source plumes.

Seigneur et al. (1984a) make a number of suggestions for improvement/evaluation for their model. In addition to these, sensitivity tests in which NMOC/NO_x ratios, reactivity, diurnal mixing height and emission patterns are varied would appear to be useful. Evaluation and (if necessary) development of a point source model is of interest for two reasons: (a) to help test the extent to which conclusions arising from the Seigneur and Scire (1985b) models can be generalized, and (b) to have a more specific treatment of specific sources which may be subject to requirements under O_3, acid deposition or visibility regulatory programs.

5. Available VOC and NO_x control technology and the associated costs should be reviewed systematically for various source categories. If strategies incorporating NO_x reductions gain more widespread use, the number and diversity of potential solutions to the O_3 problem will increase. Greater attention needs to be paid to the economic implications of different strategies to help select the most cost effective one for an urban area.

5.5.2 Implications for Ozone Strategies

1. Our review suggests that VOC control continues to be the preferable strategy for reducing peak O_3 levels to the NAAQS downwind of cities having NMOC/NO_x ratios below about 10:1.

2. Cities having NMOC/NO_x ratios about 10:1 or greater could, in some cases, reduce their downwind peak O_3 concentrations to levels below the NAAQS most effectively by using some NO_x reductions in addition to VOC control strategies. To determine whether a VOC-only or a VOC strategy with some NO_x control is most effective or feasible, a case-by-case investigation would be required. The most expeditious strategy depends on a number of factors, including atmospheric dilution, reactivity of the NMOC mix, severity of the O_3 levels and cost/feasibility of controls.

The information we have reviewed implies that benefits of NO_x control may increase (a) as NMOC/NO_x ratios increase; (b) as NMOC reactivity increases; (c) as NO_x concentrations during the daylight hours decrease and (d) as the severity of the city's peak downwind O_3 concentrations decreases. However, a strategy incorporating substantial NO_x controls has higher risks associated with it than does one emphasizing VOC controls with or without small reductions in NO_x. That is, in an area with a moderate to severe O_3 problem, a strategy incorporating large NO_x reductions, may result in conditions in the most heavily populated areas deteriorating before they improve. Further, such a strategy may have several practical problems such as those described in paragraph 4 below. Thus, city-specific analyses (i.e., grid modeling) considering the above factors would be necessary to justify adoption of a strategy emphasizing NO_x controls. In particular, such analyses should include some means of assurance that the NO_x strategy will not cause violations of the NAAQS in heavily populated areas where no violations presently occur. In the absence of a city-specific assessment of a strategy emphasizing NO_x control vs. one emphasizing VOC control, a VOC reduction strategy would appear to be the approach of choice for reducing O_3. Whether or not a VOC strategy might best include some NO_x reductions should be considered on a case-by-case basis using city-specific EKMA or the Urban Airshed photochemical grid model.

3. Strategies which encourage increases in NO_x emissions should not be permitted, since such strategies may increase the potential for acid deposition, visibility degradation and threaten NAAQS for NO_2.

4. Our review suggests that in some cities NO_x control will not assist in reducing O_3 levels, whereas in others it may have merit. Consequences of NO_x control with regard to O_3 appear to be much more of a "mixed bag" than VOC control. Thus, in contrast to VOC controls, NO_x control programs which are consistent with flexible city-specific strategies would appear most promising.

(a) For example, mobile source programs, such as I/M, which can be applied selectively should prove useful.

(b) Efforts to develop NSPS, define BACT for new sources and RACT for existing sources of NO_x should be useful. However, application of BACT/RACT to sources of NO_x as an O_3 control strategy should be more selective than is the case for sources of VOC.

5. On the basis of our review, we conclude that high O_3 concentrations ($\geq$ 0.12 ppm) observed in rural areas occur almost entirely as the result of impacts from urban plumes. We further conclude that strategies which are effective in reducing peak O_3 in urban plumes should generally also reduce high O_3 concentrations further downwind. Therefore, we believe the existing strategy of giving higher priority to controlling VOC emissions in urban areas is fundamentally sound. It may be desirable, however, to reconsider the 200,000 population cutoff currently used to distinguish "urban" from "rural". Our review suggests that, although not a widespread major problem, emissions from population centers smaller than 200,000 can result in perceptible increases in O_3 levels. Therefore, it would be prudent to conduct studies to see whether particular localities (<200,000 pop.) are causing violations of the O_3 NAAQS and, if so, consider the need for additional emission reductions. Determination of whether NO_x or VOC strategies in small cities or "rural" areas would be preferable would be most appropriately made on a case-by-case basis.

6. We do not believe that the available evidence concerning overnight transport of NO_2/PAN and subsequent reaction of NO_2 leading to second day rural O_3 formation to levels above the NAAQS is particularly convincing. Nevertheless some increase in rural NO_x, and hence, rural O_3, due to urban VOC control strategies cannot be ruled out at this time. In cases where NMOC and NO_x reduction result in equal reductions in first day peak O_3 levels, the NO_x

strategy would probably result in greater reductions in O_3 further downwind. Counterbalancing this however, are findings which suggest that (1) transported NMOC can last in measurable quantities for more than a day and (2) transported NMOC can make the task of attaining the NAAQS in downwind NO_x rich areas (i.e., cities) more difficult if those cities employ VOC control strategies. On balance, we do not believe that concern over O_3 far downwind is a sufficient basis for choosing an urban NO_x strategy over a VOC strategy. However, it may help justify incorporation of some selective NO_x controls in strategies emphasizing VOC reduction.

7. If there is a local problem in complying with a present or future NO_2 NAAQS, reduction in NO_x emissions should be beneficial, unless the resulting NO_2 is formed by reaction with O_3 and is limited by the available O_3. NMOC reductions appear to have small, ambiguous benefits on peak NO_2 and no apparent benefit on mean NO_2.

8. The limited information available to us implies that VOC control has a small, ambiguous and nonlinear effect on formation of acidic species. Controlling VOC may have some beneficial effects so far as improving regional visibility is concerned. However, such improvements are likely to be small, because only certain NMOC species form aerosol and such secondary organic aerosol is not thought to lead to major regional visibility attenuation.

9. NO_x control appears likely to reduce HNO_3 concentrations. Reducing NO_x has an ambiguous effect on H_2SO_4 formation according to best available estimates. In the absence of high SO_2 or $SO_4^=$, reduction of NO_x may improve regional visibility. Thus, we believe that NO_x control could be potentially beneficial in the western U.S., both with regard to reduction of ambient acid species concentrations and improvement in regional visibility. In the eastern

U.S., reduction in NO_x will most likely result in little improvement in regional visibility unless substantial reductions in $SO_4^=$ first occur. In the East, some reduction in acidic species concentrations is most likely if NO_x reductions are implemented, provided the assumptions we have made are appropriate.

The preceding findings suggest that strategies to reduce O_3 may not be entirely compatible with strategies to reduce acid deposition and/or to improve visibility. In order to minimize adverse impacts on cities with strategies emphasizing VOC control to reduce O_3, the following set of selective controls should be considered for controlling sources of NO_x in strategies to reduce acid deposition or to improve visibility:

(a) NO_x sources in cities opting for a strategy emphasizing NO_x reduction to reduce O_3;

(b) elevated point sources of NO_x in western rural areas;

(c) elevated point sources of NO_x in eastern rural areas;

(d) elevated point sources of NO_x in western cities; and

(e) elevated point sources of NO_x in eastern cities.

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